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Performance Test Results and Comparative Data for Designated Reference and Equivalent Methods for Ozone

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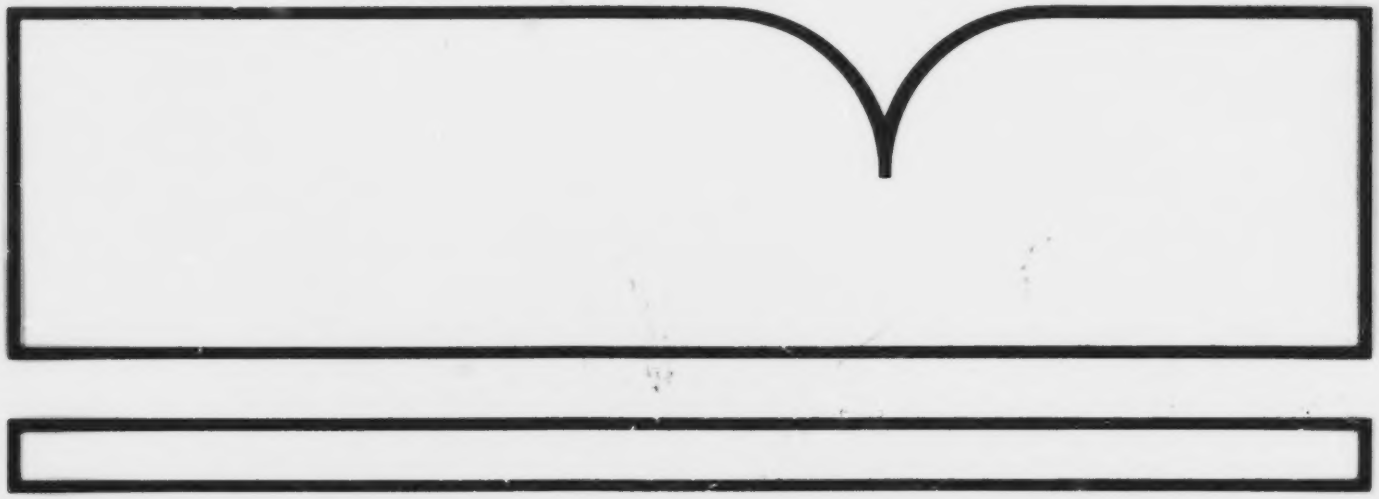

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PERFORMANCE TEST RESULTS AND COMPARATIVE DATA FOR DESIGNATED REFERENCE AND EQUIVALENT METHODS FOR OZONE

by

Frederick W. Sexton
Raymond M. Michie, Jr.
Environmental Quality Assurance Department
Research Triangle Institute
Research Triangle Park, NC 27709

Frank F. McElroy
Vinson L. Thompson
Jack A. Bowen
Methods Standardization Branch
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Contract Numbers: 68-02-2714, 68-02-3222

EPA Project Officer: Frank F. McElroy
Quality Assurance Division
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency

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Research Triangle Park, NC 27709

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Under Part 53 of Title 40 of the Code of Federal Regulations (40 CFR Part 53), the U.S. Environmental Protection Agency designates specific ambient monitoring methods and analyzers as reference or equivalent methods acceptable for use in National Air Monitoring Stations (NAMS), State and Local Air Monitoring Stations (SLAMS), and Prevention of Significant Deterioration (PSD) monitoring. Such designation requires that extensive performance test of the analyzer be carried out by the manufacturer (or other applicant) prior to designation. After designation, EPA carries out further tests of the analyzer. These EPA tests include performance tests as well as comparative tests to evaluate the performance, reliability, and operational peculiarities of the analyzer with respect to other analyzers monitoring the same pollutant.

This report summarizes both the manufacturer's predesignation test results and the EPA post designation test results of the currently designated ozone analyzers. The data is presented in tabular and graphic form, with specific conclusions concerning any particular analyzer left to the reader.

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This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, has responsibility for: assessment of environmental monitoring technology and systems; implementation of agency wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency, including the Office of Air, Noise and Radiation, the Office of Toxic Substances, and the Office of Enforcement.

Assessment of environmental monitoring technology is performed in part by the Quality Assurance Division. Through the Equivalency Testing Program, automated analyzers are evaluated to ensure that specified performance criteria are met. This document is the first in a series that summarizes performance test results and comparative data obtained during analyzer evaluations. The series will document evaluations of analyzers that monitor ambient air for ozone, oxides of nitrogen, suflur dioxide, and carbon monoxide.

ABSTRACT

Under Part 53 of the Title 40 of the Code of Federal Regulations (40 CFR Part 53), the U.S. Environmental Protection Agency designates specific ambient monitoring methods and analyzers as reference or equivalent methods acceptable for use in National Air Monitoring Stations (NAMS), State and Local Air Monitoring Stations (SLAMS), and Prevention of Significant Deterioration (PSD) monitoring. Such designation requires that extensive performance test of the analyzer be carried out by the manufacturer (or other applicant) prior to designation. After designation, EPA carries out further tests of the analyzer. These EPA tests include performance tests as well as comparative tests to evaluate the performance, reliability, and operational peculiarities of the analyzer with respect to other analyzers monitoring the same pollutant.

This report summarizes both the manufacturer's predesignation test results and the EPA post designation test results of the currently designated ozone analyzers. The data are presented in tabular and graphic form, with specific conclusions concerning any particular analyzer left to the reader.

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SECTION 1

INTRODUCTION

Under Part 53 of Title 40 of the Code of Federal Regulations (40 CFR Part 53), the U.S. Environmental Protection Agency (EPA) designates specific ambient monitoring methods and analyzers as acceptable for use in National Air Monitoring Stations (NAMS), State and Local Air Monitoring Stations (SLAMS), and Prevention of Significant Deterioration (PSD) monitoring, among other monitoring applications. These methods are designated as reference methods or equivalent methods, depending on whether or not the method employs a particular measurement principle and calibration procedure specified for each pollutant in 40 CFR Part 50. A list of all currently designated methods is available from the Quality Assurance Division (QAD) or from the Quality Control Coordinator at any EPA Regional Office.

Commercial analyzer models are designated on the basis of a reference or equivalent method application submitted by the manufacturer (or other applicant). This application must show that an analyzer representative of the analyzer model meets the following criteria:

1. It has been tested according to specific test procedures;

2. It meets prescribed minimum performance specifications; and

3. It meets certain other requirements such as having a suitable calibration procedure and an adequate operation and instruction manual.

Any designated analyzer model should meet the requirements mentioned above. However, these analyzer models may differ considerably in design, features, reliability, measurement principle, ease of operation, and level of performance above the required minimum. These factors allow for intelligent selection of the best or most appropriate analyzer for a particular application.

The Methods Standardization Branch (MSB) of the Environmental Monitoring Systems Laboratory (EMSL) at Research Triangle Park, NC, is responsible for EPA's reference and equivalent method designation program for ambient air monitoring methods. In this capacity, MSB acquires performance data and other information on these methods, particularly on the various commercial analyzer models that have been designated as reference or equivalent methods.

To summarize this information and make it available to those who may find it beneficial in selecting analyzers, MSB, with the assistance of the Research Triangle Institute, has prepared this report on designated methods for ozone. Other reports are planned on SO_2, CO, and NO_2.

The information presented in this report is derived from the following sources:

1. The predesignation test data submitted by the applicant,

2. Postdesignation tests conducted by MSB,

3. Reports or comments from analyzer users, and

4. Other pertinent information as needed.

This information is factual, to the best of our knowledge, and is presented with a minimum of interpretation, leaving readers to draw their own conclusions.

The predesignation test data were extracted from the application for designation submitted by the applicant (usually the analyzer manufacturer) and were thus obtained from tests conducted at the applicant's own laboratory or test site. These tests must be conducted in accordance with the explicit test procedures specified in 40 CFR Part 53. Results must then be calculated and interpreted according to the perscribed specifications.

The postdesignation tests conducted by MSB are part of an ongoing postdesignation test program and may include one or more of the following types:

1) Phase I tests are laboratory performance tests similar to the predesignation tests required by 40 CFR Part 53;

2) Phase II tests simulate actual use conditions and serve to intercompare designated methods; and

3) Phase III tests are special purpose tests for specific individual analyzers used when unique needs or circumstances arise.

Postdesignation test results are the major source of information in this report and are described in detail in Section 2. The tests were conducted either by Quality Assurance Division (QAD) personnel or by a contractor, under QAD direction, who had no contractual or financial association with any commercial manufacturers of designated analyzers. Because of resource limitations, there may be substantial delays in completing the postdesignation tests of an analyzer model following its designation as a reference or equivalent method.

MSB encourages analyzer users to submit comments that might be of interest to others using or contemplating purchase of a designated analyzer. Such comments, particularly negative comments, are more valuable if they are

accompanied by supporting data, records, or other documentation. Finally, pertinent information from other sources, such as other EPA groups, testing laboratories, and manufacturers will also be included when available.

The information in this report is based on files maintained by MSB for each designated method. Publication of an updated report will be considered whenever significant new information is available. Additional information on any aspect of the report may be obtained from MSB. The report is not intended to recommend or endorse any particular analyzer over others. MSB welcomes any comments on the usefulness of these reports or suggestions for improvement. Our address is on the front page; our phone numbers are as follows:

Commercial:	(919)	541-2622
	(919)	541-2665
FTS:		629-2622
		629-2665

SECTION 2

POSTDESIGNATION TESTING

Because the primary predesignation testing of an analyzer is carried out by the manufacturer or other applicant, it is EPA'S general policy to perform followup performance tests on the analyzer after designation. These tests are referred to as postdesignation tests and are of three types: Phase I, Phase II, and Phase III. Phase I and II tests are described below. Phase III tests include any special tests or special circumstances not covered by Phase I and II and are conducted only where deemed necessary or appropriate.

The postdesignation tests are usually carried out on an analyzer purchased by EPA through normal procurement procedures. Occasionally, an analyzer purchased prior to designation is returned to the manufacturer for upgrading to designated status. Commercially unavailable analyzers have to be borrowed for the tests. The manufacturer is always made aware of the testing and that the test analyzer obtained will be assumed to be representative of the model. Because of the complex nature of most analyzers, variability in performance from one instrument to another can be expected. Even though all analyzers must be within the required specifications, this potential variability must be kept in mind when the test results in this summary are considered and compared with those of other analyzers.

PHASE I TESTS

General Description

Phase I tests are laboratory performance tests that are conducted in accordance with the same test procedures and specifications required for the applicant's predesignation tests. The one exception is that fewer trials (usually four) are performed for each test parameter. All calibrations, test apparatus, pollutant standards, test procedures, test atmospheres, and test documentation are as specified in 40 CFR Part 53. An individual report containing more detailed information on the Phase I test for each analyzer tested is available from MSB.

Analyzers to be Phase I tested are set up and allowed to operate for several weeks prior to actual testing. During this startup period, preliminary calibrations and linearity checks are performed to verify proper operation. In the event that unusual behavior such as nonlinearity or inoperability due to a major malfunction is identified, the manufacturer is notified.

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The manufacturer is encouraged to become involved throughout the startup period in order to identify potential problems prior to testing. If a failure occurs during testing, however, the manufacturer is notified and given the opportunity to repair the analyzer. At the conclusion of the test, all failures and manufacturer involvement are documented and reported.

Data Interpretation

The Phase I test results for each analyzer are shown in tables 1-9 along with the EPA performance specifications and the applicants' own predesignation test data (as reported in the equivalency application). The results reported are averages of several trials for each parameter (usually four trials for the EPA Phase I data, and seven for the applicant's predesignation data). The test results must generally be less than (or within) the EPA performance specifications shown for an analyzer to achieve designation, and except for the lower detectable limit, these results are comparable in a relative sense from one instrument to another. The manufacturer's advertized or claimed performance specifications, however, may not be directly comparable to the test data or to other analyzers since manufacturers may choose to define their performance specifications, or how they are measured, differently. The various EPA performance parameters are described briefly below along with pertinent comments. See 40 CFR 53 for the formal definitions of the performance parameters and the prescribed test procedure for each.

Noise--

Noise refers to short-term deviations in the analyzer output that are not caused by changes in the input concentration. Noise is measured at both 0% and 80% of the upper range limit and is the standard deviation of 25 readings taken at 2 min intervals. Normally, this value will be slightly less than the average deviation from the mean value and is usually much less than the peak-to-peak noise.

Lower Detectable Limit (LDL)--

The lower detectable limit (LDL) is the smallest pollutant concentration that produces an output change of at least twice the noise level. The test does not determine the actual LDL; it only verifies that the output signal at an input concentration of 0.01 ppm is at least two times the 0 ppm noise level. Therefore, the value reported is usually close to 0.01 ppm and must be greater than twice the noise level. An output signal significantly lower than 0.01 ppm may indicate a nonapparent negative zero offset or other low level response problems.

Interference Equivalent--

The interference equivalent is the relative degree of unwanted response caused by other compounds present in the ambient air sample. The reported values should not be interpreted as the actual error to be expected in the measurements because the test concentrations of most of the interferents are higher than those normally encountered in ambient air. However, the values for water and CO_2 do represent the approximate error that may result when the calibration gases are dry and/or free of CO_2.

Zero Drift (12 h)--

The 12 h zero drift is the maximum change in continuous output response to zero input concentration over a 12-h period of unadjusted operation. The 12 h zero drift includes any peak-to-peak noise component so it may be higher than the 24 h zero drift.

Zero Drift (24 h)--

The 24 h zero drift is the net change in response to zero input concentration between two points in time ≈24 h apart during unadjusted analyzer operation and includes changes in ambient temperature, line voltage, or both. The 24 h zero drift tends to be sometimes positive, sometimes negative; hence the average would be misleadingly low. Therefore, the average of the absolute values of the analyzer's daily drift is reported in tables 1-9 as a more meaningful value.

Span Drift (20% URL)--

The span drift at 20% URL (upper range limit) is the net change in response to an input concentration of ≈20% of the URL between two points in time ≈24 h apart, during unadjusted analyer operation and including changes in ambient temperature, line voltage, or both. Because of the 20% URL concentration level, the reported value represents a combination of both zero drift and span drift over the period. The average of the absolute values is reported.

Span Drift (80% URL)--

In the span drift at 80% URL, an input concentration of ≈80% URL is used. The 80% URL span drift is calculated without a correction for zero drift; therefore it may be higher or lower than the actual change in the slope of the calibration curve. Again, the average of the absolute values of the individual daily results is reported.

Lag Time--

Lag time is the time required to observe the first change in response due to a sudden change in input concentration.

Rise Time--

Rise time is the time (not including the lag time) required for the response to reach 95% of its final value after a sudden increase in the input concentration.

Fall Time--

Fall time is the time (excluding lag time) for the response to decrease to 5% of its previous value when the input concentration is suddenly changed to 0 ppm.

Long lag, rise, or fall times generally do not adversely affect measurements expressed as hourly averages and may even be beneficial where concentrations fluctuate rapidly. However, long response times may be an annoyance or source of error during calibration and zero and span drift adjustment.

Precision--

Precision is the variation in the response value to repeated measurements at 20% and 80% URL of the same upscale pollutant concentration, reported as the standard deviation. The reported precision is a measure of the repeatability of an analyzer's reading when alternately approached from lower and higher concentrations.

PHASE II TESTS

General Description

Phase II tests are intended to test analyzers in a more or less typical ambient monitoring configuration where their stability, reliability, general performance, and operational peculiarities can be observed, recorded and compared. The tests are conducted simultaneously on a group of analyzers during a period of several months. All analyzers measure the same pollutant in the ambient air which is sampled from a common manifold. The ambient pollutant concentrations are sometimes augmented in the manifold with artificially generated pollutant to increase the concentration readings.

Unless otherwise specified, the Phase II tests are carried out at EPA's Durham Air Monitoring Demonstration Facility (DAMDF) located in the urban industrial commercial area of Durham, NC. Ambient air samples for the analyzers are drawn from an intake on the building roof and distributed by an all glass, power ventilated manifold system. Pollutant levels are augmented, when appropriate, with a special manifold which has two inlet ports, a 1 L mixing chamber, 12 sampling ports, and an outlet flowmeter used to determine the supplemental pollutant flow rate. All sample air contains at least 90% unaltered ambient air. The analyzers' inlets are connected to the manifold via Teflon® particulate filters and either 3 mm (1/8 in) or 6 mm (1/4 in) Teflon® tubing, depending on the analyzer flow rate. The sample lines are kept as short as practical.

All test analyzers are installed, calibrated, operated, and maintained in accordance with the manufacturer's operation/instruction manual and good monitoring practice. Analyzers receive a multipoint calibration initially and once per month during the test period. Two point zero and span checks are made two or three times per week, with zero adjustments only if the zero response is not within ±3% of fullscale response from nominal, and span adjustments only if the span (slope of calibration curve) changes by more than ±7% from nominal.

Zero air is obtained from filtered ambient air by appropriate drying and chemical scrubbing. Calibration and span gases are obtained by techniques such as dilution of high concentration cylinder gases, permeation devices and gas phase titration. Ozone concentrations are generated by ultraviolet radiation and are traceable to a UV standard; all other pollutant concentrations are traceable to National Bureau of Standards Standard Reference Materials (NBS-SRM).

Analyzer readings are normally recorded at 1 min intervals using a monitor Labs 9300 data acquisition system. One-hour averages (50 min minimum) are automatically calculated and transfered to magnetic tape. Zero and span

responses are also recorded on the tape. The tapes are read into a Hewlett-Packard 9831A Desk Top computer for verification, editing, corrections as necessary, and calculation of the various statistical comparisons. (See Section 3 for information concerning the alternate data acquisition system used during the ozone phase II tests.)

Data Interpretation

The Phase II test results and other data are presented in Section 3 as a series of figures for each analyzer. The figures in each analyzer's series are discussed below in their order of occurrence. First is a typical multipoint calibration curve for the analyzer, showing five or more points spaced over the full scale range. When possible, the recorder zero is offset to ≈5% of full scale in order to observe any negative zero drifts. The span is normally adjusted to a slope of ≈200 (scale %/ppm) for a 0 to 0.5 ppm range. The actual zero (intercept, A) and span (slope, M) shown on the curves are calculated by least squares regression from the actual calibration response data. The correlation coefficient is a measure of the analyzer's linearity and of the variability in the calibration concentrations.

The chronological records of the zero and span drift for each analyzer are shown next in the series of figures. Zero drift is plotted in absolute units (ppb) while the span drift is plotted as the cumulative % difference in the span slope from the nominal slope (not percent-of-scale change in an arbitrary span concentration). Both zero and span drifts are total accumulated drifts except where manual adjustments are explicitly indicated. The drifts are referenced to the nominal intercept (5% of scale) and nominal slope (200) represented by the horizontal, dashed lines. Also shown are the nominal adjustment limits for zero (±3% of full scale) and span (±7%). Adjustments made because the response exceeded the nominal drift limits for zero or span are indicated by (●). Additional adjustments made during routine calibrations are indicated by arrows situated on the x-axis. It was often not possible to adjust the zero and span to the exact nominal values desired because of the nature of the controls. The drift plots are intended mainly for visual comparison among the various analyzers.

The next several figures present comparisons of the differences in hourly ambient air readings between subject analyzers and the average of simultaneous readings from other analyzers. Corrections for zero and span drifts are made before the data are compared. The comparison is shown in the form of a frequency distribution indicating both numerically and graphically the frequency (number of hours out of the total test period) of the occurrence of each discrepancy versus its magnitude and sign.

Also given are the correlation coefficient, the mean difference (bias), the standard deviation of the differences, and the number of absolute differences > 20 ppb; all of these are statistics calculated with respect to the differences between the hourly readings of the subject analyzer and the average of the corresponding hourly readings from the other analyzers in the test group. When an analyzer exhibits a marked change in performance during the course of the study (such as after correction of a malfunction), two or more figures are included to illustrate the "before and after" performance.

Additional figures show the same type of frequency distribution discussed above but without periodic zero and span corrections; all hourly averages for the subject analyzers are based on the original calibration curve. The reference data from the analyzers on which the comparison is based is still corrected for zero and span drift. Comparison of the data in corresponding sets of frequency distributions, particularly the mean difference and the standard deviation of the differences, illustrates the effect of making periodic zero and span corrections to ambient monitoring data. Usually, the agreement of the hourly readings (bias, spread, or both) is improved by the periodic zero and span adjustments, and the practice is generally recommended where possible. The performance of several of the ozone analyzers, however, is such that there is little or no improvement between the corrected and uncorrected data.

It is apparent that improved comparisons of the analyzers could have been made if all of the analyzers had been tested simultaneously. Subsequent Phase II tests will use simultaneous testing and will include more sophisticated statistical comparisons.

SECTION 3

TEST RESULTS AND DATA FOR DESIGNATED O_3 ANALYZERS

PHASE 1 TESTS

This section contains summary information pertaining to Phase I tests performed on seven ozone analyzers. Also discussed are specific aspects of the tests resulting in unusual analyzer behavior and manufacturers' involvement. The seven analyzers tested and the dates of their testing are as follows:

Meloy 350-2R Monitor Labs 8410E Bendix 8002	May 1977 to September 1977
Dasibi 1003-AH Philips PW 9771 Beckman 950-A McMillan 1100-2	November 1977 to April 1978

Calibration Technique

At the time of the Phase I Tests, supersession of the 1% NBKI ozone calibration procedure as outlined in Appendix D of 40 CFR Part 50 was under consideration. Therefore, a tentative calibration procedure based on gas phase titration (GPT) with excess NO as specified in the Federal Register, Vol 41, No 195, October 6, 1976 was used instead. This procedure was used to calibrate an ozone working standard (a stable ozone generator). Excess nitric oxide was supplied by NBS-SRM 1684a at 92.06 ppm NO in nitrogen.

"Overshoot" Phenomenon

During the testing of the ozone analyzers, an "overshoot" condition was sometimes encountered. Overshoot refers to a peculiar response from an analyzer when it's input was changed from a low to a high ozone concentration. The analyzer's initial response often exceeded the span concentration by as much as 10%. After 0.5 to 1 h, the response decreased and tended to stabilize at the span concentration. A significant problem occurred when an excessive amount of time (as much as 2 to 6 h) was required for the response to stabilize at the final level.

Of the seven analyzers tested, only the Beckman 950-A and the MEC 1100-2 exhibited overshoot during Phase I tests. These analyzers were tested simultaneously with the Philips PW 9771 and the Dasibi 1003-AH, neither of

which showed any overshoot. Thus, the condition could not have been caused by the test apparatus. The overshoot condition seemed to be predominant in the analyzers operating on Ethychem® (see the description of the ozone/ethylene chemiluminescent measurement principle in Appendix A.)

Beckman's response to the problem was to send a representative to troubleshoot the analyzer. The representative replaced the photomultiplier tube, which somewhat lessened the overshoot condition but did not correct it entirely. Further failures during Phase I testing were attributed to a combination of the overshoot condition plus a temperature sensitivity condition. Beckman sent another representative who investigated both the temperature sensitivity and the overshoot problem. After several days of troubleshooting, the temperature sensitivity condition was resolved but the overshoot condition was still present, although it was not severe enough to cause any Phase I test failures. No overshoot difficulties were encountered during Phase II tests.

When McMillan was contacted concerning the overshoot condition in the MEC 1100-2 analyzer, their representative stated that the overshoot was typical. In Phase I testing, a marginal failure occurred in the 80% span drift test. The allowed ±5.0% drift was exceeded on one occasion with a total drift of -5.08%. The actual span drift was significantly less, but the overshoot condition caused an inaccurate drift measurement by preventing quick, stable readings of precision test points. No overshoot difficulties were encountered during Phase II tests.

As noted in the subsections on each analyzer, overshoot did not seem to be noticeable during the ambient measurements. The results show that all analyzers correlated well. Even during calibration and span checks, overshoot did not seem to be a problem. The overshoot effect may appear only when the analyzer samples dry gas for many hours, as in the Phase I tests. Other user comments and experiences on the prevalence of this overshoot condition would be particularly helpful.

Test Results

Tables 1-9 summarize the Phase I laboratory performance test results for each analyzer and compare these data with EPA specifications and the manufacturer's test results.

PHASE II TESTS

Due to limited availability of analyzers and to data processing limitations at the time, three Phase II tests were scheduled with three analyzers per test. Since there were seven analyzers to be tested, the Bendix 8002 was chosen as a reference in all three tests with the remaining six analyzers segregated in groups of two. The test groups and their dates for Phase II testing are as follows:

Group 1: Bendix 8002
Meloy 350-2R
Monitor Labs 8410E
Test period: September 1977 to December 1977

Group 2: Bendix 8002
Philips PW 9771
Dasibi 1003-AH
Test period: May 1978 to September 1978

Group 3: Bendix 8002
McMillan 1100-2
Beckman 950-A
Test period: June 1978 to September 1978

Although three separate Phase II tests were performed, the same test procedures were duplicated in each test. A primary UV calibration standard (UV photometer) was used to verify the ozone working standard throughout the tests, with the frequency of calibrations, zero and span checks remaining the same. Data resulting from the tests indicate the function of the Bendix 8002 was stable throughout the studies.

The test results indicate that the ozone analyzers tested are among the most stable and reliable of continuous air monitoring analyzers. Zero drift was virtually nonexistent, span drifts were low (a few percent over several weeks) for most analyzers, and malfunctions were minimal. The comparative data also show generally excellent performance, with very high correlation coefficients, mean differences of < 2 or 3 ppb, and standard deviation of < 3 ppb (tight distributions) in most cases.

Alternate Data Acquisition System

During this Phase II test of the ozone analyzers, the Monitor Labs data acquisition system was not yet available. Consequently, test data were collected on strip chart records, which were read manually. The hourly averages were then entered into a Hewlett Packard 9821A Desk Top computer for statistical calculations.

Test Results

Phase II test results for each tested analyzer are shown in a series of figures contained in the various analyzer subsections.

Figure 1. Bendix Model 8002 Ozone Analyzer (RFOA-0176-007). The Bendix Corporation, Environmental and Process Instruments Division, P.O. Box 831, Lewisburg, WV 24901.

General Description

The Bendix Model 8002 ozone analyzer operates on the ozone/ethylene chemiluminescent detection measurement principle (see Appendix A). The instrument offers a choice of seven ranges from 0 to 0.01 ppm up to 0 to 1.0 ppm full scale and three time constants: 1, 10, and 40 seconds. An internal ozone generator for span checks is standard, as is a photomultiplier thermoelectric cooler designed to maintain the detector at 5 °C (41 °F). The instrument's reference method designation applies when operated on the 0 to 0.5 ppm range at a time constant setting of 40 seconds, in ambient temperatures of 20 to 30 °C (68 to 86 °F), and at a line voltage of 105 to 125 Vac. Operation is approved for both 100% ethylene and Ethychem® or equivalent ethylene/CO_2 blend (see Appendix A).

TABLE 1. BENDIX 8002 LABORATORY PERFORMANCE TEST RESULTS

Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.005	0.000	0.000
Noise – 80% URL	ppm	0.005	0.001	0.001
Lower detectable limit	ppm	0.01	0.010	0.013
Interferents	ppm			
H_2O		±0.02	<0.001	<0.001
H_2S		±0.02	<0.001	0.000
CO_2		±0.02	0.006	0.000
Total		≤ 0.06	0.007[d]	<0.001[d]
Zero drift – 12 hr	ppm	±0.02	0.001[d]	0.001[d]
Zero drift – 24 hr	ppm	±0.02	0.001[d]	0.001[d]
Span drift – 20% URL	%	±20.0	2.45[d]	2.80[d]
Span drift – 80% URL	%	±5.0	2.33[d]	2.59[d]
Lag time	min	20	0.3	0.1
Rise time	min	15	2.0	1.1
Fall time	min	15	2.0	1.5
Precision – 20% URL	ppm	0.010	0.001	0.000
Precision – 80% URL	ppm	0.010	0.001	0.001

[a]From EPA equivalency regulations, 40 CFR Part 53.
[b]Average, from manufacturer's application for equivalency determination.
[c]Average, from EPA Phase I postdesignation tests, S/N 3017488.
[d]Average of absolute values.

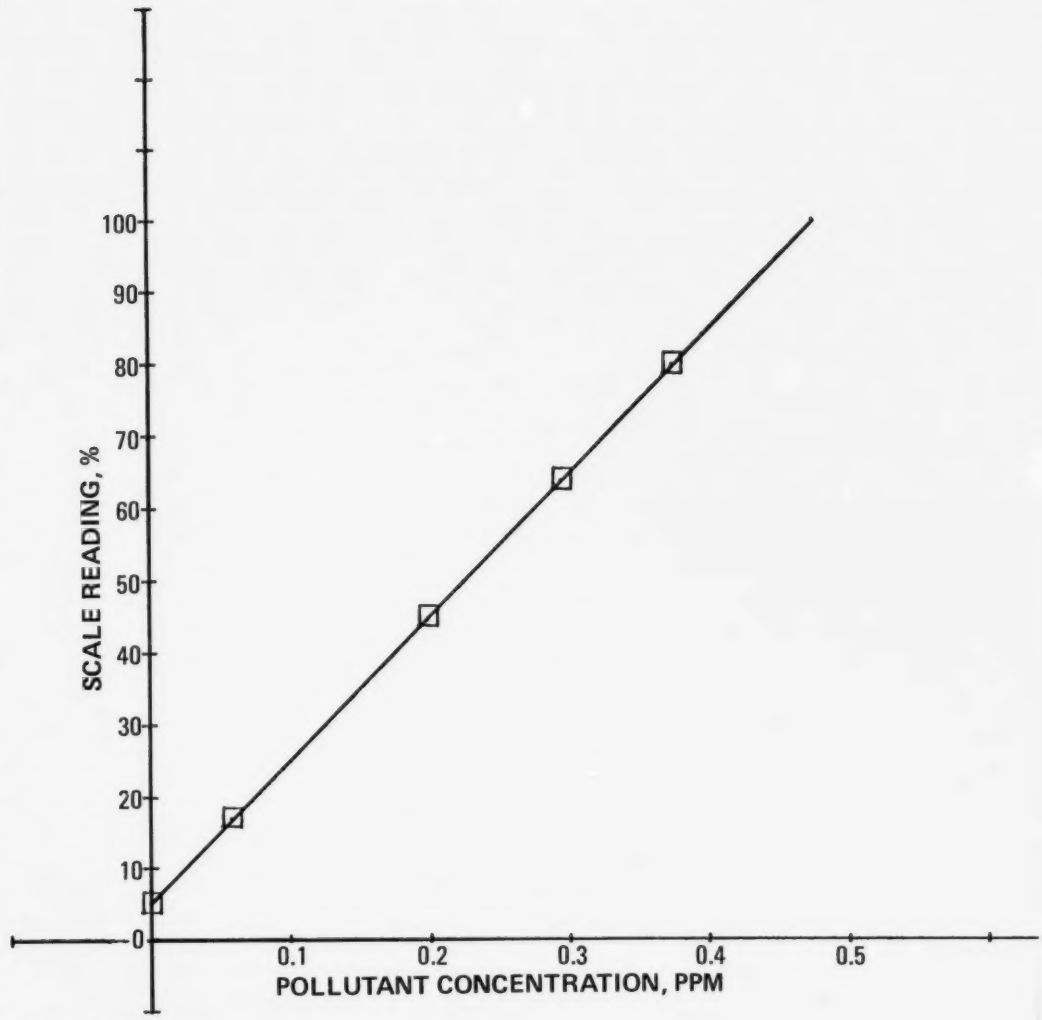
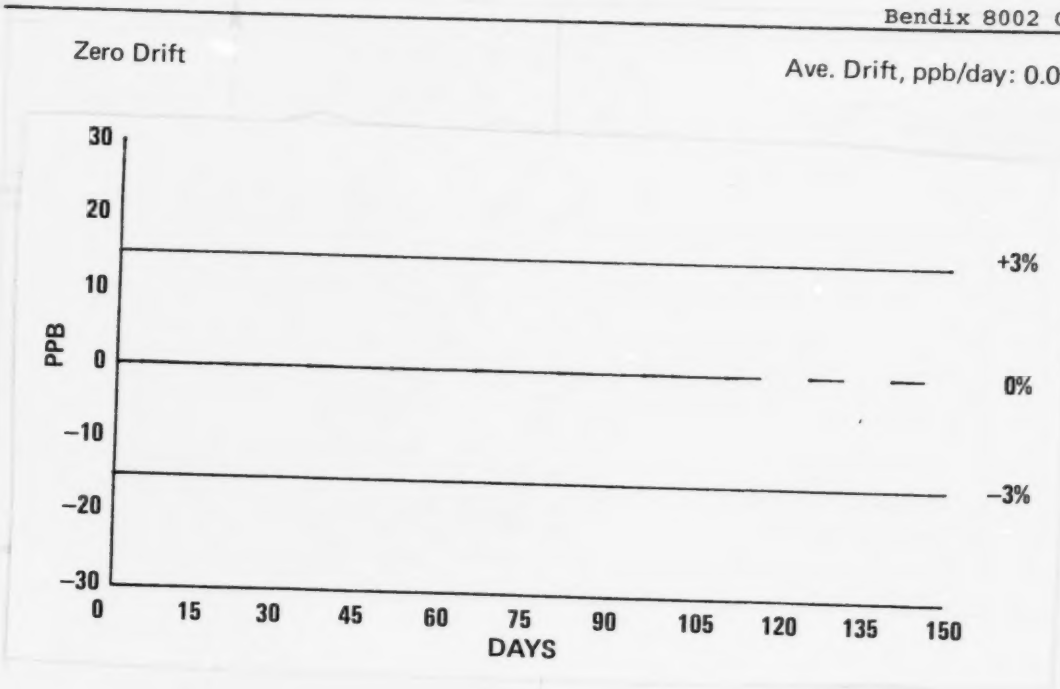


Figure 2. Typical calibration curve for Bendix 8002. Date: 9/25/78; curve drawn according to Y=MX+A where slope (M)=199.511, zero (A)=5.211; correlation coefficient (R)=1.000.



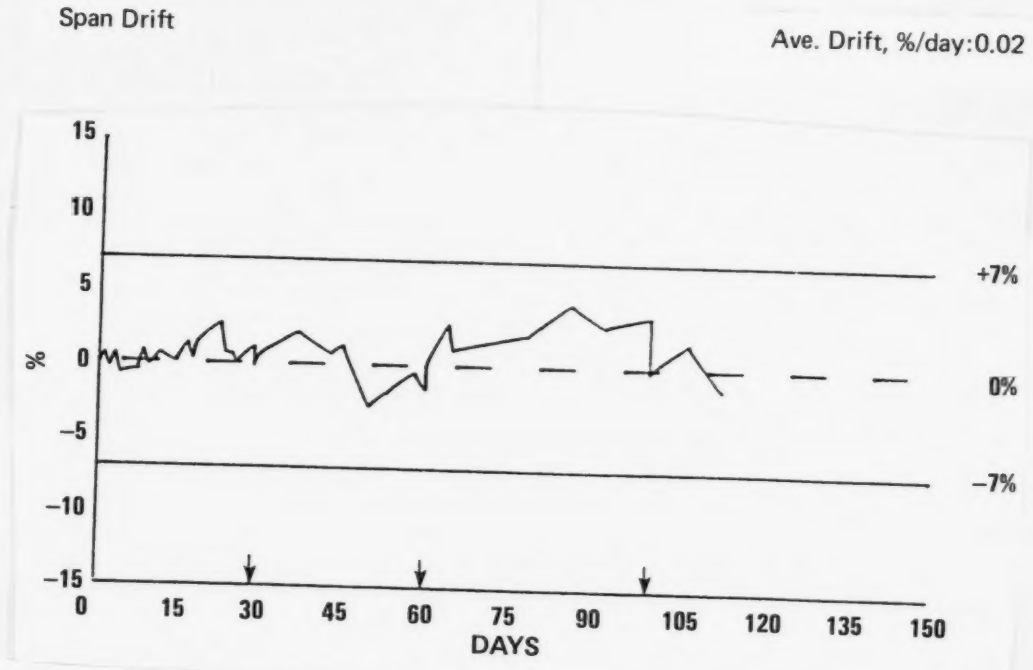
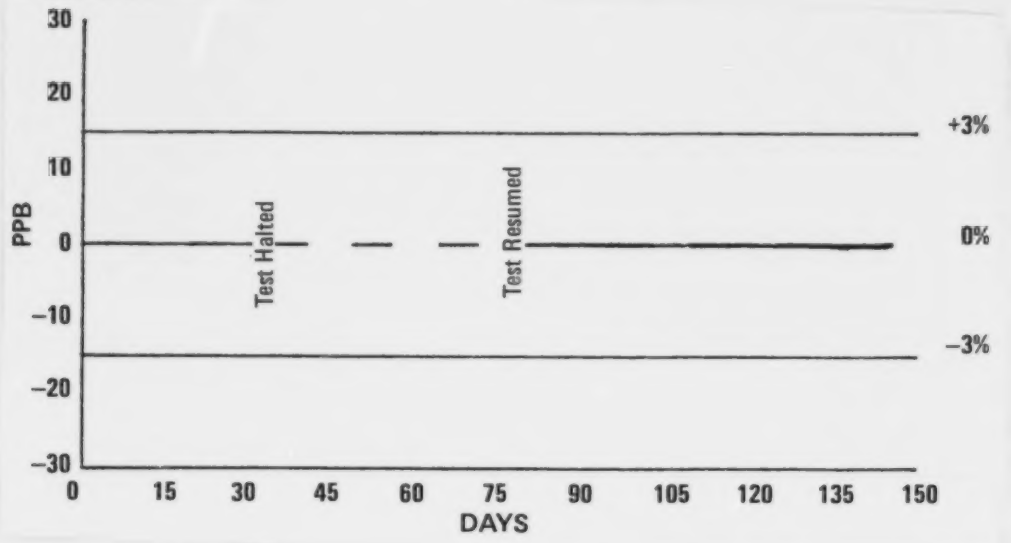


Figure 3. Zero and span drift data during group 1 Phase II Test. Nominal zero: 5.0% scale; nominal slope: 200%/ppm.

Zero Drift

Ave. Drift, ppb/day: 0.00



Span Drift

Ave. Drift, %/day: −0.05

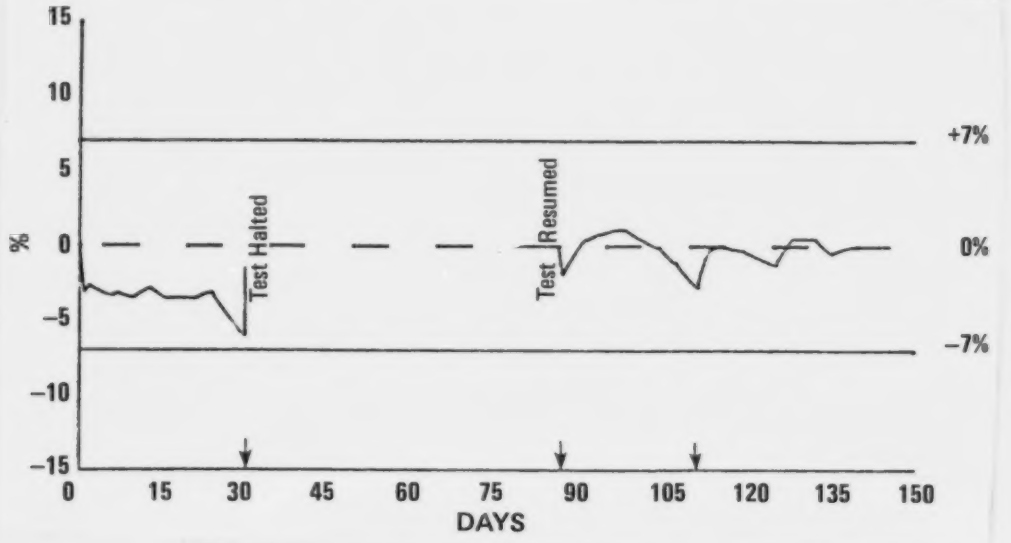
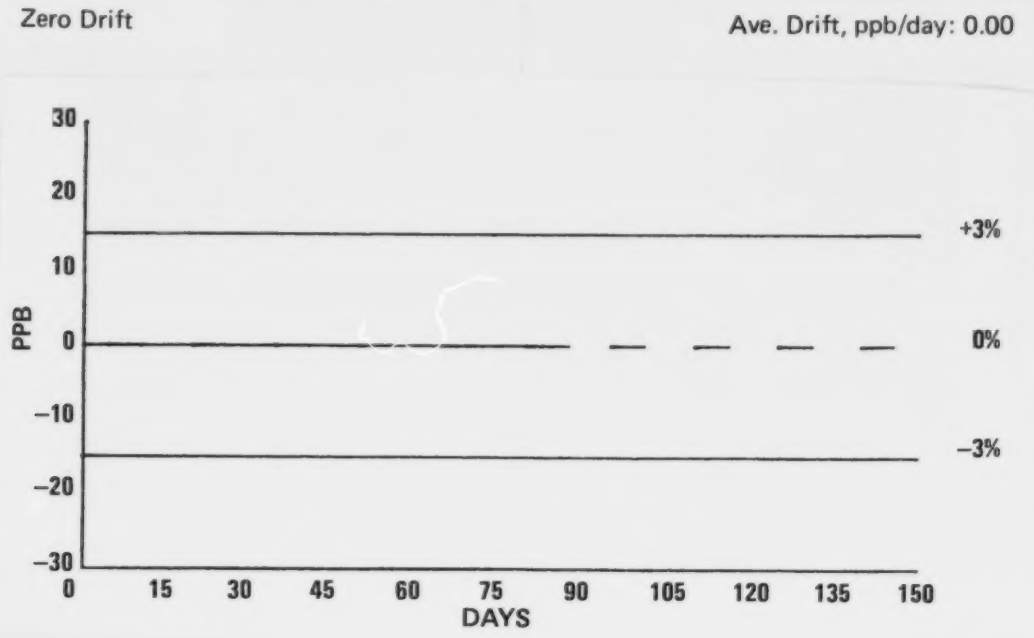


Figure 4. Zero and span drift data during Group 2 Phase II Test. Nominal zero: 5.0% scale; nominal slope: 200%/ppm.



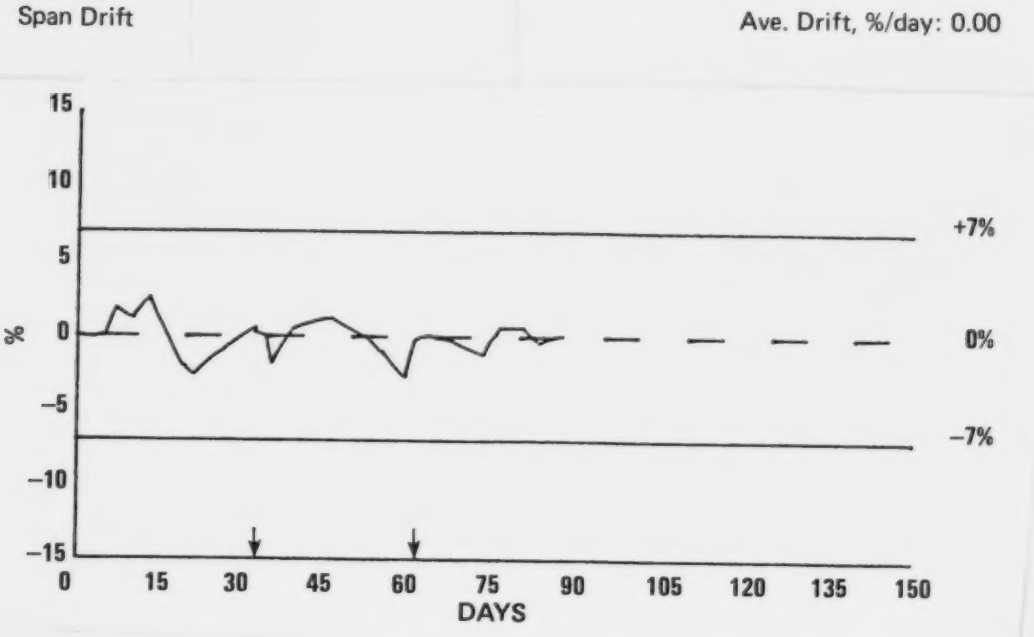


Figure 5. Zero and span drift data during Group 3 Phase II Test. Nominal zero: 5.0% scale; nominal slope: 200%/ppm.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN ppb:

ppb Range	Data Pairs	
<-19	1	X
-19 to -17	1	X
-17 to -15	6	X
-15 to -13	5	X
-13 to -11	6	X
-11 to -9	12	X
-9 to -7	0	
-7 to -5	49	XX
-5 to -3	87	XXX
-3 to -1	505	XXXXXXXXXXXXXXXXX
-1 to 1	1,118	OOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOO
1 to 3	408	XXXXXXXXXXXXXX
3 to 5	66	XX
5 to 7	15	X
7 to 9	6	X
9 to 11	0	
11 to 13	0	
13 to 15	0	
15 to 17	0	
17 to 19	0	
>19	1	X

Number of Data Pairs: 2,286;
Correlation Coefficient: 0.99;
Mean Difference (ppb): -0.36;
Standard Deviation of Differences (ppb): 2.48;
Number of Absolute Differences > 20: 2;
Number of Test Days: 99.

Figure 6. Frequency distribution of differences in hourly ambient air readings between the Bendix 8002 and average of simultaneous readings from Meloy 350-2R and Monitor Labs 8410E during Group 1 Phase II Test. All readings corrected for zero and span drift.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN ppb:

ppb Range	Data Pairs	
≤19	0	
-19 to-17	0	
-17 to-15	0	
-15 to-13	0	
-13 to-11	0	
-11 to-9	0	
-9 to-7	0	
-7 to-5	27	XX
-5 to-3	56	XX
-3 to-1	389	XXXXXXXXXXXX
-1 to 1	1,249	OOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOO
1 to 3	491	XXXXXXXXXXXXXXX
3 to 5	64	XX
5 to 7	6	X
7 to 9	4	X
9 to 11	0	
11 to 13	0	
13 to 15	0	
15 to 17	0	
17 to 19	0	
>19	0	

Number of Data Pairs: 2,286;
Correlation Coefficient: 0.99;
Mean Difference (ppb): 0.06;
Standard Deviation of Differences (ppb): 1.73;
Number of Absolute Differences > 20: 0;
Number of Test Days: 99.

Figure 7. Frequency distribution of differences in hourly ambient air readings between the Bendix 8002 and average of simultaneous readings from Meloy 350-2R and Monitor Labs 8410E during Group 1 Phase II Test. Bendix 8002 readings not corrected for zero and span drift.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN ppb:

ppb Range	Data Pairs	
⩽19	0	
-19 to-17	0	
-17 to-15	0	
-15 to-13	0	
-13 to-11	5	X
-11 to-9	13	X
-9 to-7	0	
-7 to-5	155	XXXXXXXX
-5 to-3	367	XXXXXXXXXXXXXXXXXXX
-3 to-1	750	XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
-1 to 1	415	OOOOOOOOOOOOOOOOOOOO
1 to 3	137	XXXXXXX
3 to 5	31	XX
5 to 7	4	X
7 to 9	5	X
9 to 11	1	X
11 to 13	0	
13 to 15	1	X
15 to 17	0	
17 to 19	0	
>19	0	

Number of Data Pairs: 1,884;
Correlation Coefficient: 0.99;
Mean Difference (ppb): -1.91;
Standard Deviation of Differences (ppb): 2.46;
Number of Absolute Differences > 20: 0;
Number of Test Days: 88.

Figure 8. Frequency distribution of differences in hourly ambient air readings between the Bendix 8002 and the average of simultaneous readings from Philips PW 9771 and Dasibi 1003-AH during Group 2 Phase II Test. All readings corrected for zero and span drift.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN ppb:

ppb Range	Data Pairs	
≤19	0	
-19 to-17	0	
-17 to-15	0	
-15 to-13	0	
-13 to-11	6	X
-11 to-9	20	X
-9 to-7	0	
-7 to-5	167	XXXXXXXXX
-5 to-3	367	XXXXXXXXXXXXXXXXXXX
-3 to-1	750	XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
-1 to 1	409	OOOOOOOOOOOOOOOOOOOO
1 to 3	129	XXXXXXX
3 to 5	25	X
5 to 7	6	X
7 to 9	4	X
9 to 11	0	
11 to 13	1	X
13 to 15	0	
15 to 17	0	
17 to 19	0	
>19	0	

Number of Data Pairs: 1,884;
Correlation Coefficient: 0.99;
Mean Difference (ppb): -2.02;
Standard Deviation of Differences (ppb): 2.48;
Number of Absolute Differences > 20: 0;
Number of Test Days: 88.

Figure 9. Frequency distribution of differences in hourly ambient air readings between the Bendix 8002 and the average of simultaneous readings from Philips PW 9771 and Dasibi 1003-AH during Group 2 Phase II Test. Bendix 8002 readings not corrected for zero and span drift.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN ppb:

ppb Range	Data Pairs	
≤19	0	
−19 to−17	0	
−17 to−15	0	
−15 to−13	1	X
−13 to−11	0	
−11 to−9	0	
−9 to−7	0	
−7 to−5	79	XXXXX
−5 to−3	286	XXXXXXXXXXXXXXXX
−3 to−1	657	XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
−1 to 1	677	OOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOO
1 to 3	217	XXXXXXXXXXXXX
3 to 5	42	XXX
5 to 7	7	X
7 to 9	2	X
9 to 11	0	
11 to 13	0	
13 to 15	0	
15 to 17	0	
17 to 19	0	
>19	0	

Number of Data Pairs: 1,968;
Correlation Coefficient: 0.99;
Mean Difference (ppb): -1.16;
Standard Deviation of Differences (ppb): 2.20;
Number of Absolute Differences > 20: 0;
Number of Test Days: 88.

Figure 10. Frequency distribution of differences in hourly ambient air readings between the Bendix 8002 and the average of simultaneous readings from MEC 1100-2 and Beckman 950-A during Group 3 Phase II Test. All readings corrected for zero and span drift.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN ppb:

ppb Range	Data Pairs	
≤19	0	
−19 to −17	0	
−17 to −15	0	
−15 to −13	0	
−13 to −11	1	X
−11 to −9	0	
−9 to −7	0	
−7 to −5	83	XXXXX
−5 to −3	252	XXXXXXXXXXXXX
−3 to −1	696	XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
−1 to 1	692	OOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOO
1 to 3	192	XXXXXXXXXX
3 to 5	45	XXX
5 to 7	4	X
7 to 9	3	X
9 to 11	0	
11 to 13	0	
13 to 15	0	
15 to 17	0	
17 to 19	0	
>19	0	

Number of Data Pairs: 1,968;
Correlation Coefficient: 0.99;
Mean Difference (ppb): -1.17;
Standard Deviation of Differences (ppb): 2.14;
Number of Absolute Differences > 20: 0;
Number of Test Days: 88.

Figure 11. Frequency distribution of differences in hourly ambient air readings between the Bendix 8002 and the average of simultaneous readings from MEC 1100-2 and Beckman 950-A during Group 3 Phase II Test. Bendix 8002 readings not corrected for zero and span drift.

Manufacturer's Recommended Maintenance

Operation	Frequency
Check all filters and components and replace Teflon air filter.	Weekly.
Replace zero air scrubber.	After 8 h of continuous use.
Replace ethylene filter.	When specified flow is unobtainable.
Replace ethylene cylinder.	When ethylene pressure decreases below 100 psig.
Clean evacuation pump reed valves.	When sample flow becomes erratic.
Dust instrument components.	As necessary to prevent excessive dust buildup.

Malfunctions

No malfunctions occurred during postdesignation testing.

General Comments

Both Phase I and Phase II tests were conducted using 100% ethylene; operation on Ethychem® was not tested.

During ≈1 year of Phase II testing, there were no operational problems. Principal maintenance included replacing the sample filter monthly and cleaning the rotameters when necessary.

After 30 days of Phase II testing of Group 2 analyzers, the Philips PW 9771 was shut down while awaiting new Rhodamine B pills. Rather than continuing the study on the remaining two instruments, the study was halted until the Philips was repaired. The Bendix, which was not shut down, was recalibrated when the study resumed.

MELOY MODELS OA 325-2R AND OA 350-2R

Figure 12. Meloy Models OA 325-2R (RFOA-1075-003) and OA 350-2R (RFOA-1075-004). Meloy Laboratories, Inc., Instruments & Systems Divisions, 6715 Electronic Drive, Springfield, VA 22151.

General Description

The Meloy OA 350-2R ozone analyzer operates on the ozone/ethylene chemiluminescent detection measurement principle (see Appendix A). Six concentration ranges are available from 0 to 0.01 ppm up to 0 to 10.0 ppm. Six time constants are available from 0.5 to 25.0 sec depending on the range. The instrument contains a built in ozone generator for span checks and a temperature control system to maintain the reactor and detector assemblies at 22 °C (71.6 °F). The instrument's reference designation applies when operated on the 0 to 0.5 ppm range at any time constant, with ambient temperature between 20 and 30 °C (68 to 86 °F), and with a line voltage of 105 to 125 Vac.

The Meloy OA 325-2R ozone analyzer has no internal ozone generator for span checks but is otherwise identical to the Model 350-2R. Only the 350-2R was tested.

TABLE 2. MELOY 350-2R LABORATORY PERFORMANCE TEST RESULTS

Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.005	<0.001	0.000
Noise – 80% URL	ppm	0.005	0.001	0.003
Lower detectable limit	ppm	0.01	0.010	0.013
Interferents	ppm			
H_2O		±0.02	0.001	0.000
H_2S		±0.02	0.000	0.000
CO_2		±0.02	<−0.001	<0.001
Total		≦0.06	0.001[d]	<0.001[d]
Zero drift – 12 hr	ppm	±0.02	0.001[d]	0.001[d]
Zero drift – 24 hr	ppm	±0.02	<0.001[d]	0.001[d]
Span drift – 20% URL	%	±20.0	0.48[d]	3.37[d]
Span drift – 80% URL	%	±5.0	1.25[d]	2.17[d]
Lag time	min	20	0.1	0.2
Rise time	min	15	0.4	0.8
Fall time	min	15	0.4	2.0
Precision – 20% URL	ppm	0.010	<0.001	0.001
Precision – 80% URL	ppm	0.010	0.001	0.001

[a]From EPA equivalency regulations, 40 CFR Part 53.
[b]Average, from manufacturer's application for equivalency determination.
[c]Average, from EPA Phase I postdesignation tests, S/N 5M139.
[d]Average of absolute values.

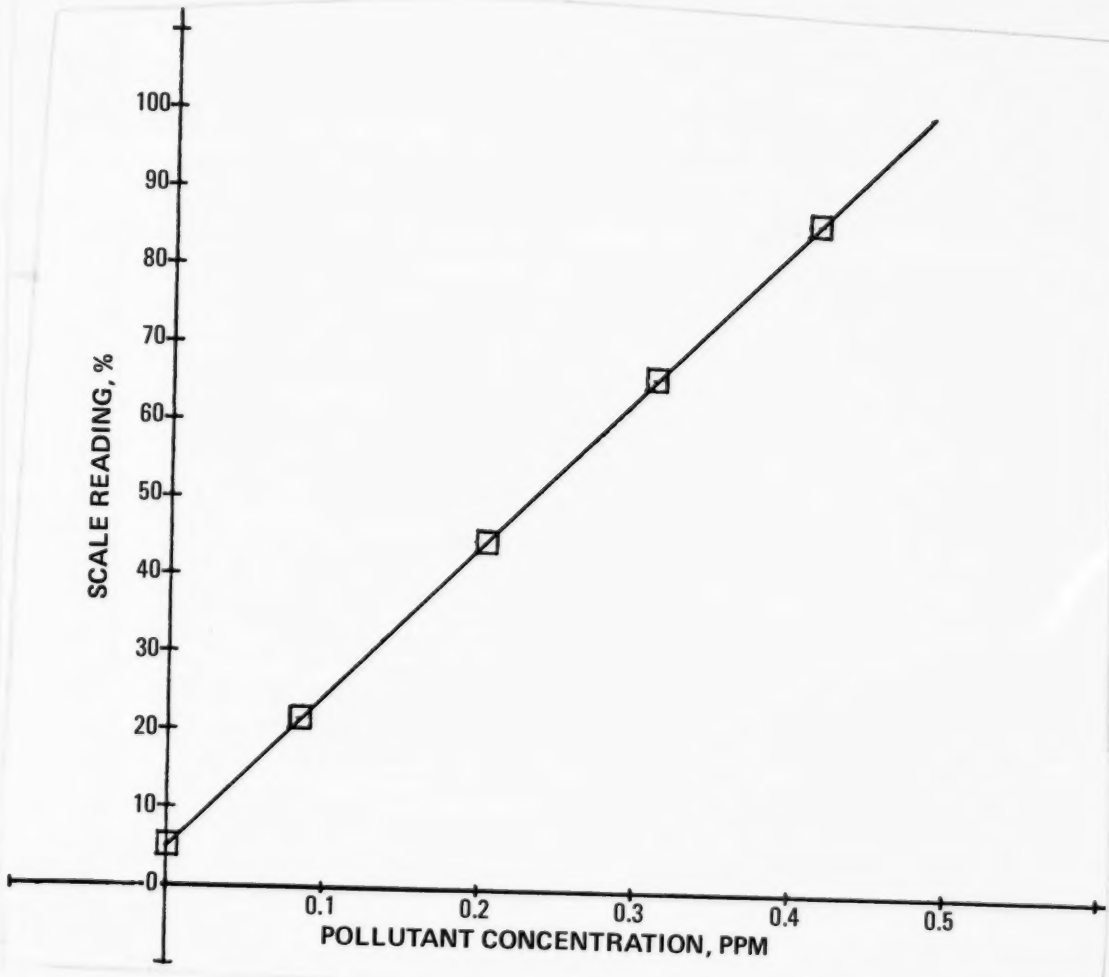
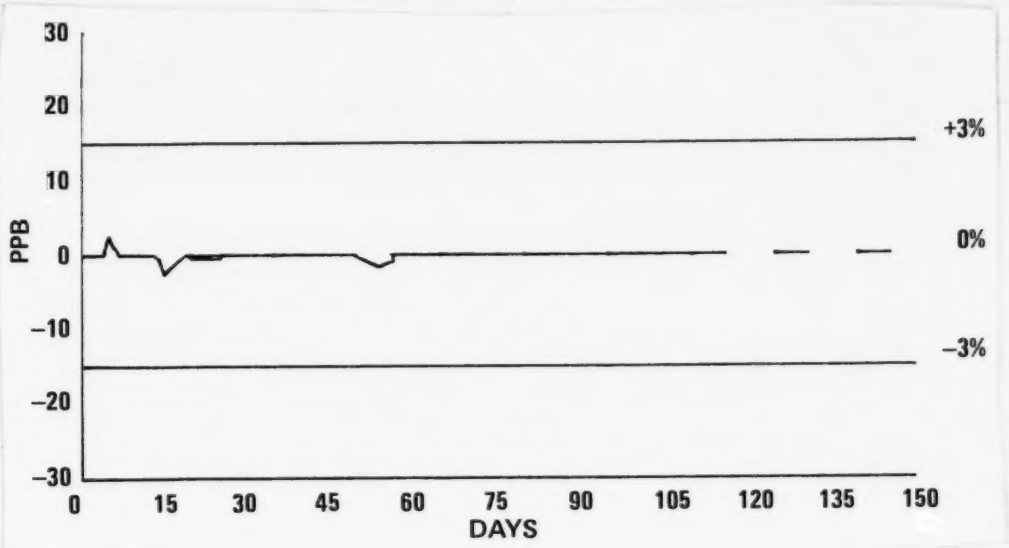


Figure 13. Typical calibration curve for Meloy 350-2R. Date: 1/9/78; curve drawn according to Y=MX+A where slope (M)=196.295, zero (A)=4.988; correlation coefficient (R)=1.000.

Zero Drift

Ave. Drift, ppb/day: –0.01



Span Drift

Ave. Drift, %/day: –0.11

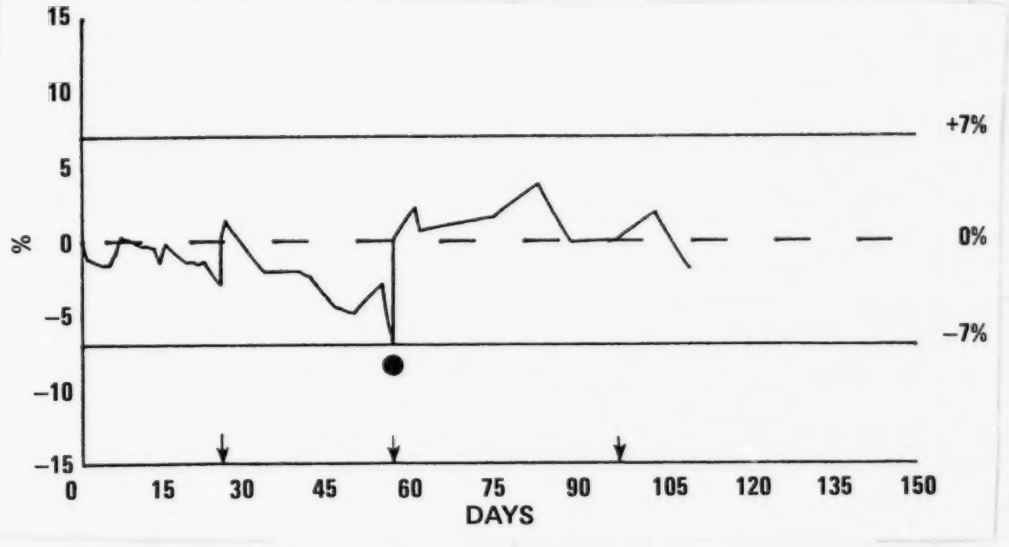


Figure 14. Zero and span drift data during Phase II Test. Nominal zero: 5.0% scale; nominal slope: 200%/ppm.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN ppb:

ppb Range	Data Pairs	
≤19	1	X
-19 to-17	0	
-17 to-15	0	
-15 to-13	0	
-13 to-11	3	X
-11 to-9	3	X
-9 to-7	0	
-7 to-5	19	X
-5 to-3	35	X
-3 to-1	328	XXXXXXXXXXX
-1 to 1	1,155	OOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOO
1 to 3	491	XXXXXXXXXXXXXXXXX
3 to 5	91	XXX
5 to 7	52	XX
7 to 9	25	X
9 to 11	8	X
11 to 13	7	X
13 to 15	0	
15 to 17	1	X
17 to 19	0	
>19	3	X

Number of Data Pairs: 2,222;
Correlation Coefficients: 0.99;
Mean Difference (ppb): 0.49;
Standard Deviation of Differences (ppb): 2.44;
Number of Absolute Differences > 20: 4;
Number of Test Days: 99.

Figure 15. Frequency distribution of differences in hourly ambient air readings between the Meloy 350-2R and the average of simultaneous readings from Bendix 8002 and Monitor Labs 8410E during Phase II Test. All readings corrected for zero and span drift.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN ppb:

ppb Range	Data Pairs	
<-19	0	
-19 to-17	0	
-17 to-15	0	
-15 to-13	0	
-13 to-11	2	X
-11 to-9	0	
-9 to-7	0	
-7 to-5	18	X
-5 to-3	29	X
-3 to-1	277	XXXXXXXXXX
-1 to 1	1,072	OOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOO
1 to 3	650	XXXXXXXXXXXXXXXXXXXXXXXX
3 to 5	130	XXXXX
5 to 7	35	X
7 to 9	8	X
9 to 11	1	X
11 to 13	0	
13 to 15	0	
15 to 17	0	
17 to 19	0	
>19	0	

Number of Data Pairs: 2,222;
Correlation Coefficient: 0.99;
Mean Difference (ppb): 0.63;
Standard Deviation of Differences (ppb): 1.89;
Number of Absolute Differences > 20: 0;
Number of Test Days: 99.

Figure 16. Frequency distribution of differences in hourly ambient air readings between the Meloy 350-2R and the average of simultaneous readings from Bendix 8002 and Monitor Labs 8410E during Phase II Test. Meloy 350-2R readings not corrected for zero and span drift.

Manufacturer's Recommended Maintenance

Operation	Frequency
Replace or clean gas flow lines.	Every 6 mo.
Clean rotameter.	Every 6 mo or when sticking.
Replace the air filter material.	Every 6 mo or as necessary.
Replace 5-µm Teflon filter element.	As necessary.
Clean the three-way solenoid switching valve (SV2).	Every 6 mo.
Replace the three-way solenoid switching valve (SV2).	Every 24 mo.
Clean the reaction chamber.	Every 3 to 12 mo or when sensitivity is reduced.
Replace the ethylene pressure regulator.	Every 24 mo.
Clean the stainless steel flow restrictor capillary.	Whenever a stable flow cannot be maintained.
Clean or replace the ethylene particulate filter.	Every 12 mo.
Clean or replace the critical orifice assembly.	Every 12 mo or when airflow becomes erratic.
Clean dilution air orifice.	Every 6 mo.
Replace dilution air orifice system.	Every 12 mo.
Clean air filter unit on ventilating fan.	As frequently as needed.

Malfunctions

The PMT temperature control card failed and was replaced by the manufacturer on 9/21/77. See General Comments.

General Comments

An erratic trace developed in the analyzer response on 9/19/77, shortly after the instrument was transferred to the Phase II test station. The manufacturer, who was notified on 9/21/77, suggested replacing the PMT temperature control card. A replacement was obtained from an SA-185-2A SO_2 analyzer and the problem was solved.

MONITOR LABS 8410E

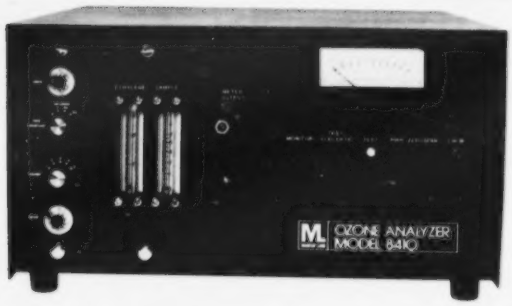


Figure 17. Monitor Labs 8410E (RFOA-1176-017). Monitor Labs, Inc., 10180 Scripps Ranch Blvd., San Diego, CA 92131.

General Description

The Monitor Labs 8410E ozone analyzer operates on the ozone/ethylene chemiluminescent detection measurement principle (see Appendix A). The light emission to the photomultiplier tube is chopped at a rate of 35 times/sec. Eight concentration ranges are available from 0 to 0.05 ppm up to 0 to 10 ppm. Four time constants are available at 1, 5, 20, and 60 seconds. The instrument's reference designation is applicable when operated on the 0 to 0.5 ppm range with a 5 second time constant, in ambient temperatures from 20 to 30 °C (68 to 86 °F), and a line voltage of 105 to 125 Vac.

TABLE 3. MONITOR LABS 8410E LABORATORY PERFORMANCE TEST RESULTS

Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.005	0.001	0.001
Noise – 80% URL	ppm	0.005	0.002	0.002
Lower detectable limit	ppm	0.01	0.009	0.012
Interferents	ppm			
H_2O		±0.02	0.000	0.000
H_2S		±0.02	<-0.001	0.001
CO_2		±0.02	<-0.001	0.000
Total		≦0.06	0.002[d]	0.001[d]
Zero drift – 12 hr	ppm	±0.02	0.001[d]	0.004[d]
Zero drift – 24 hr	ppm	±0.02	<0.001[d]	0.001[d]
Span drift – 20% URL	%	±20.0	2.26[d]	2.30[d]
Span drift – 80% URL	%	±5.0	2.87[d]	1.62[d]
Lag time	min	20	<1.0	0.2
Rise time	min	15	<1.0	0.8
Fall time	min	15	<1.0	1.5
Precision – 20% URL	ppm	0.010	0.001	0.001
Precision – 80% URL	ppm	0.010	0.001	0.001

[a]From EPA equivalency regulations, 40 CFR Part 53.
[b]Average, from manufacturer's application for equivalency determination.
[c]Average, from EPA Phase I postdesignation tests, S/N 305.
[d]Average of absolute values.

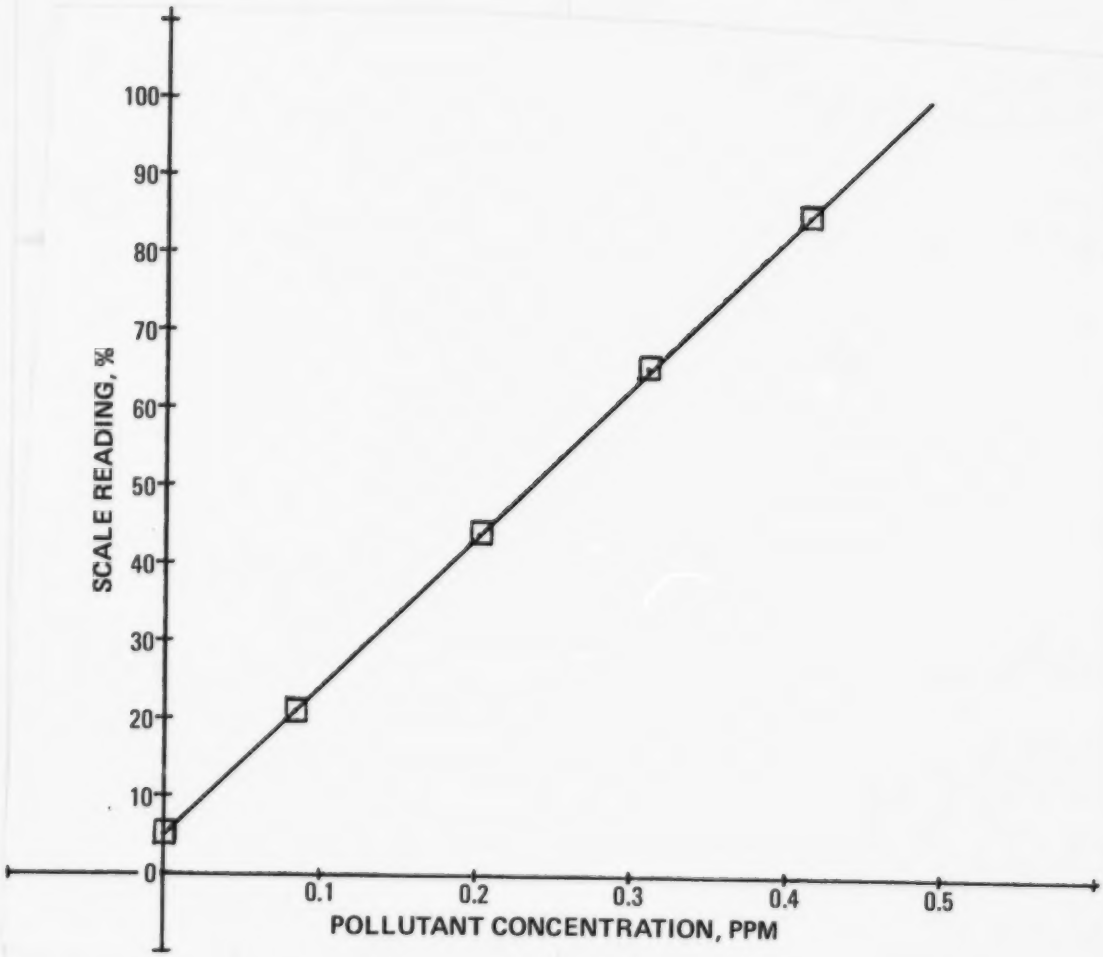
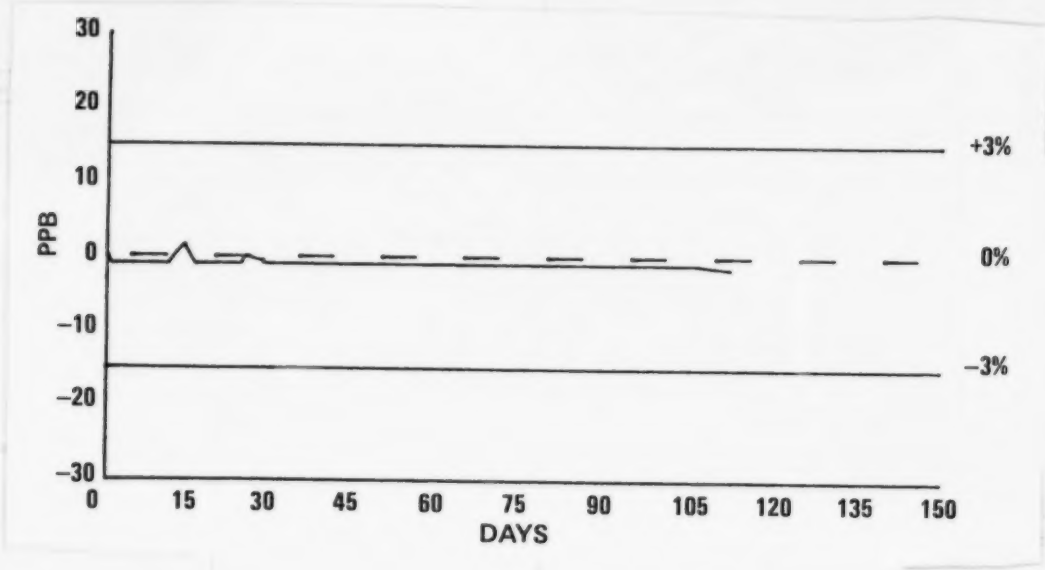


Figure 18. Typical calibration curve for Monitor Labs 8410E. Date: 1/9/78; curve drawn according to Y=MX+A where slope (M)=194.433, zero (A)=4.863; correlation coefficient (R)=1.000.

Zero Drift

Ave. Drift, ppb/day: –0.01



Span Drift

Ave. Drift, %/day: –0.09

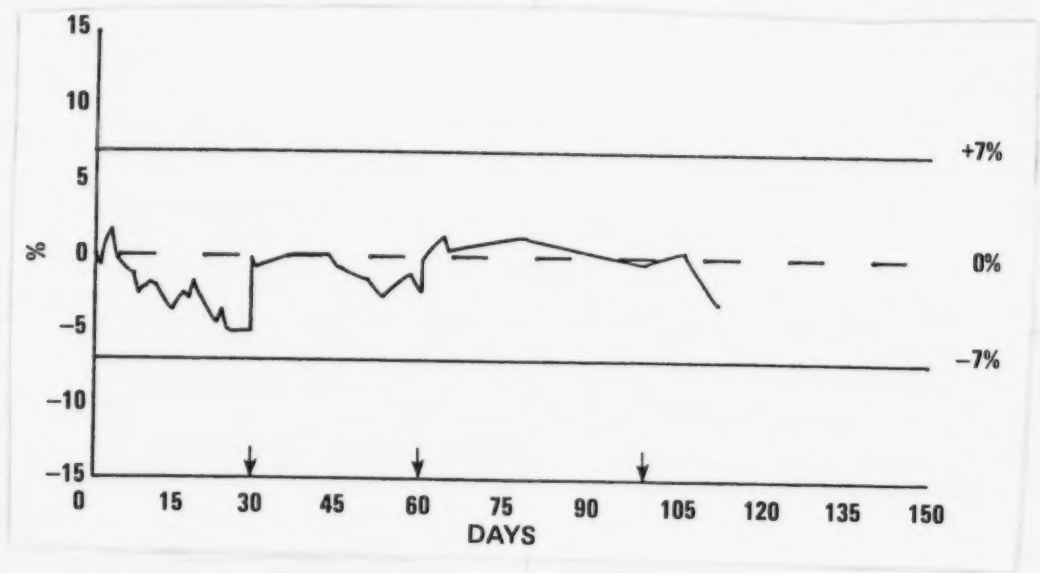


Figure 19. Zero and span drift data during Phase II Test.
Nominal zero: 5.0% scale; nominal slope: 200%/ppm.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN ppb:

ppb Range	Data Pairs	
<-19	1	X
-19 to-17	0	
-17 to-15	0	
-15 to-13	0	
-13 to-11	1	X
-11 to-9	1	X
-9 to-7	0	
-7 to-5	17	X
-5 to-3	101	XXXX
-3 to-1	572	XXXXXXXXXXXXXXXXXXXXXXXX
-1 to 1	917	OOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOO
1 to 3	227	XXXXXXXXXX
3 to 5	60	XXX
5 to 7	20	X
7 to 9	5	X
9 to 11	0	
11 to 13	2	X
13 to 15	0	
15 to 17	0	
17 to 19	0	
>19	1	X

Number of Data Pairs: 1,925;
Correlation Coefficient: 0.99;
Mean Difference (ppb): -0.41;
Standard Deviation of Differences (ppb): 2.10;
Number of Absolute Differences > 20: 2;
Number of Test Days: 99.

Figure 20. Frequency distribution of differences in hourly ambient air readings between the Monitor Labs 8410E and the average of simultaneous readings of Bendix 8002 and Meloy 350-2R during Phase II Test. All readings corrected for zero and span drift.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN ppb:

ppb Range	Data Pairs	
<-19	0	
-19 to -17	0	
-17 to -15	1	X
-15 to -13	0	
-13 to -11	0	
-11 to -9	1	X
-9 to -7	0	
-7 to -5	17	X
-5 to -3	114	XXXXX
-3 to -1	595	XXXXXXXXXXXXXXXXXXXXXXXXXX
-1 to 1	932	OOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOO
1 to 3	222	XXXXXXXXXX
3 to 5	37	XX
5 to 7	5	X
7 to 9	1	X
9 to 11	0	
11 to 13	0	
13 to 15	0	
15 to 17	0	
17 to 19	0	
>19	0	

Number of Data Pairs: 1.925;
Correlation Coefficient: 0.99;
Mean Difference (ppb): -0.59;
Standard Deviation of Differences (ppb): 1.61;
Number of Absolute Differences > 20: 0;
Number of Test Days: 99.

Figure 21. Frequency distribution of differences in hourly ambient air readings between the Monitor Labs 8410E and the average of simultaneous readings from Bendix 8002 and Meloy 350-2R during Phase II Test. Monitor Labs 8410E readings not corrected for zero and span drift.

Manufacturer's Recommended Maintenance

Operation	Frequency
Replace chassis fan.	When noisy.
Replace chopper.	When operation is sluggish or noisy.
Replace chopper motor.	When the motor fails to operate smoothly at 180 rpm.
Replace chopper drive belt.	If cracks are detected.
Inspect and clean flowmeters.	Weekly or as necessary.
Replace particulate filter.	Every 30 days, maximum.
Clean pneumatic lines and filters.	When response becomes sluggish.
Clean the reaction chamber.	When response becomes sluggish.
Examine and clean vacuum pump.	When pump vacuum falls to < 17 in Hg.
Clean and replace fan filters.	As necessary.
Clean ISOFLO module.	When flow rates and output become irregular.
Test for leaks.	Prior to any troubleshooting.

Malfunctions

The Chopper motor failed twice, on 6/2/77 and 12/11/77. See General Comments.

General Comments

The chopper motor failed on June 2, 1977 after operating at the EPA test facility for 26 days. Shipping time for a replacement motor was ≈3 weeks. This second chopper motor failed on December 11, 1977 after operating for 126 days.

The ethylene rotameter float became stuck on several occasions; a sharp rap to the rotameter released the ball.

PHILIPS PW 9771

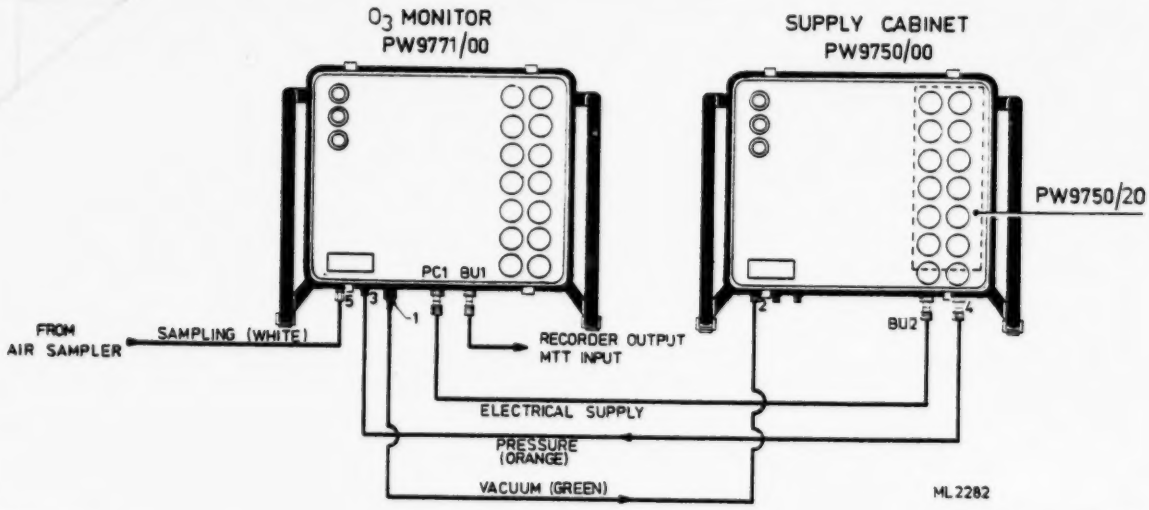


Figure 22. Philips PW 9771 (EQOA-0777-023). Philips Electronic Instrument, Inc., 85 McKee Drive, Mahwah, NJ 07430.

General Description

The Philips PW 9771 ozone analyzer operates on the ozone/rhodamine B chemiluminescent detection principle (see Appendix A). The instrument is contained in two cabinets: one houses the sample pump and air movement controls and the other houses the electronics and the detector. The instrument contains internal zero and span controls and can be operated on a 0 to 0.167 ppm range or a 0 to 0.5 range. The instrument's equivalent designation is applicable when operated on the 0 to 0.5 ppm range at 105 to 125 VAC and 20 to 30 °C (68 to 86 °F) temperature range.

TABLE 4. PHILIPS PW 9771 LABORATORY PERFORMANCE TEST RESULTS

Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.005	<0.001	0.001
Noise – 80% URL	ppm	0.005	0.003	0.005
Lower detectable limit	ppm	0.01	0.008	0.012
Interferents	ppm			
CO_2		±0.02	0.000	<- 0.001
H_2O		±0.02	0.000	<- 0.001
H_2S		±0.02	0.000	0.000
Total		≦ 0.06	0.000[d]	0.001[d]
Zero drift – 12 hr	ppm	±0.02	0.000[d]	0.001[d]
Zero drift – 24 hr	ppm	±0.02	0.000[d]	0.001[d]
Span drift – 20% URL	%	±20.0	0.67[d]	1.28[d]
Span drift – 80% URL	%	±5.0	1.76[d]	0.69[d]
Lag time	min	20	1.0	0.4
Rise time	min	15	1.1	3.0
Fall time	min	15	0.4	1.5
Precision – 20% URL	ppm	0.010	0.000	0.001
Precision – 80% URL	ppm	0.010	0.001	0.002

[a]From EPA equivalency regulations, 40 CFR Part 53.
[b]Average, from manufacturer's application for equivalency determination.
[c]Average, from EPA Phase I postdesignation tests, S/N D685F.
[d]Average of absolute values.

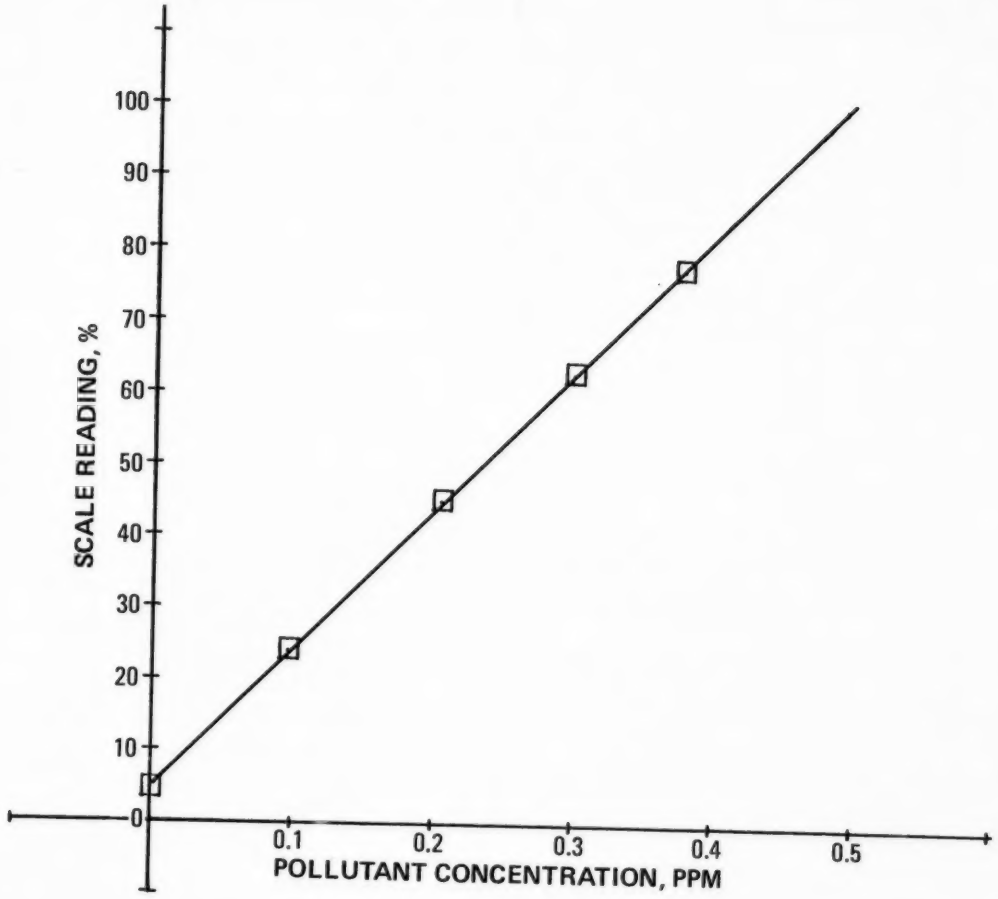
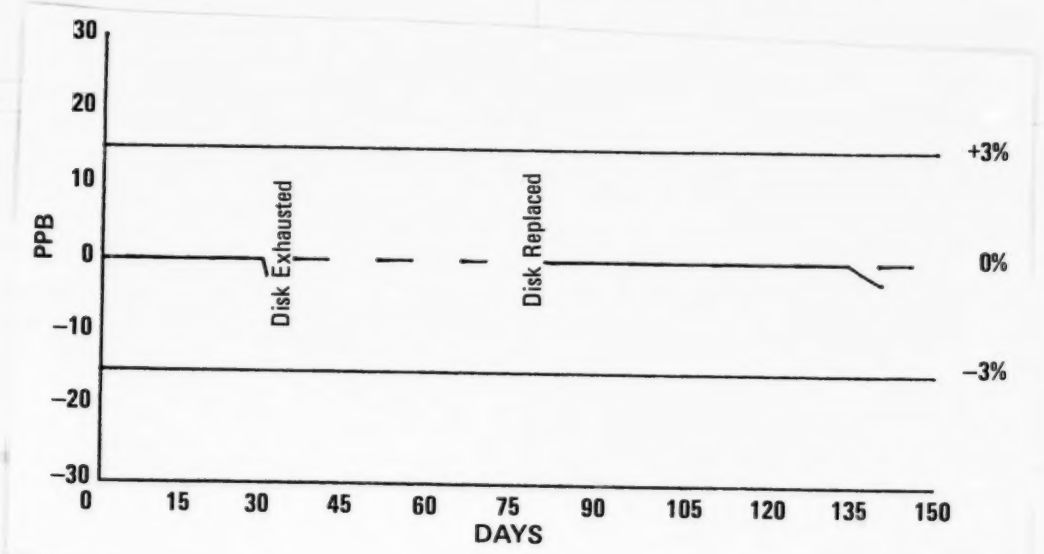


Figure 23. Typical calibration curve for Philips PW 9771. Date: 9/27/78; curve drawn according to Y=MX+A where slope (M)=193.625, zero (A)=4.927; correlation coefficient (R)=1.000.

Zero Drift

Ave Drift, ppb/day: –0.03



Span Drift

Ave. Drift, %/day: –0.05

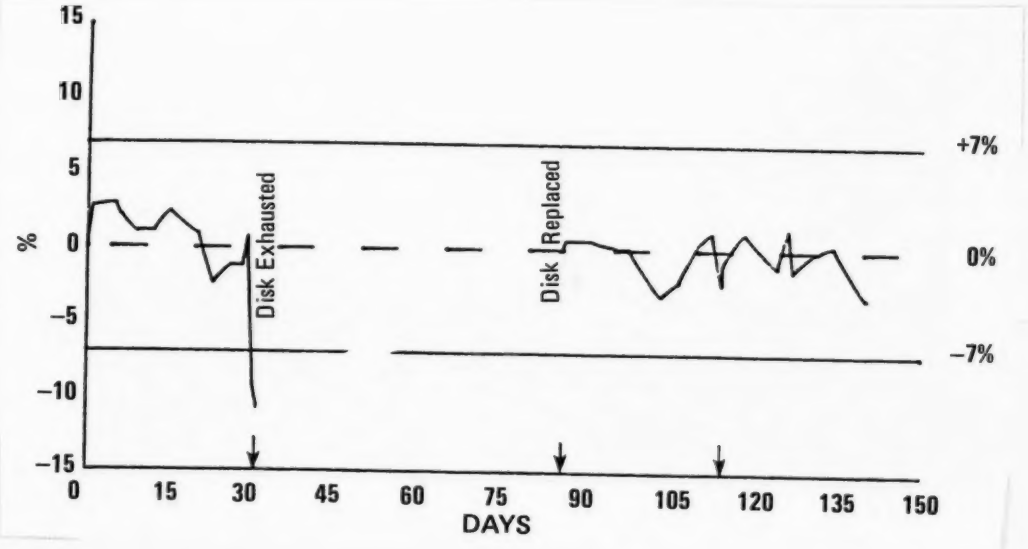


Figure 24. Zero and span drift data during Phase II Test. Nominal zero: 5.0% scale; nominal slope: 200%/ppm.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN ppb:

ppb Range	Data Pairs	
<-19	0	
-19 to-17	0	
-17 to-15	0	
-15 to-13	1	X
-13 to-11	0	
-11 to-9	2	X
-9 to-7	0	
-7 to-5	12	XXX
-5 to-3	17	XXXXX
-3 to-1	58	XXXXXXXXXXXXXXXX
-1 to 1	135	OOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOO
1 to 3	143	XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
3 to 5	131	XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
5 to 7	106	XXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
7 to 9	47	XXXXXXXXXXXXX
9 to 11	11	X
11 to 13	2	X
13 to 15	5	X
15 to 17	1	X
17 to 19	1	X
>19	0	

Number of Data Pairs: 672;
Correlation Coefficient: 0.99;
Mean difference (ppb): 2.63;
Standard Deviation of Differences (ppb): 3.68;
Number of Absolute Differences > 20: 0;
Number of Test Days: 32.

Figure 25. Frequency distribution of differences in hourly ambient air readings between the Philips PW 9771 and the average of simultaneous readings from Bendix 8002 and Dasibi 1003-AH during Plase II Test prior to exhaustion of Rhodamine B disc. All readings corrected for zero and span drift.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN ppb:

ppb Range	Data Pairs	
<-19	0	
-19 to -17	0	
-17 to -15	0	
-15 to -13	1	X
-13 to -11	0	
-11 to -9	2	X
-9 to -7	0	
-7 to -5	11	XXX
-5 to -3	18	XXXXX
-3 to -1	57	XXXXXXXXXXXXXXX
-1 to 1	133	OOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOO
1 to 3	150	XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
3 to 5	140	XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
5 to 7	85	XXXXXXXXXXXXXXXXXXXXX
7 to 9	58	XXXXXXXXXXXXXX
9 to 11	15	XXXX
11 to 13	1	X
13 to 15	0	
15 to 17	0	
17 to 19	1	X
>19	0	

Number of Data Pairs: 672;
Correlation Coefficient: 0.99;
Mean Difference (ppb): 2.57;
Standard Deviation of Differences (ppb): 6.28;
Number of Absolute Differences > 20: 0;
Number of Test Days: 32.

Figure 26. Frequency distribution of differences in hourly ambient air readings between the Philips PW 9771 and the average of simultaneous readings from Bendix 8002 and Dasibi 1003-AH during Phase II prior to exhaustion of Rhodamine B disc. Philips PW 9771 readings not corrected for zero and span drift.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN ppb:

ppb Range	Data Pairs	
<-19	0	
-19 to-17	0	
-17 to-15	0	
-15 to-13	0	
-13 to-11	0	
-11 to-9	2	X
-9 to-7	0	
-7 to-5	19	XX
-5 to-3	38	XXXX
-3 to-1	169	XXXXXXXXXXXXXXXXXX
-1 to 1	266	OOOOOOOOOOOOOOOOOOOOOOOOOOOO
1 to 3	353	XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
3 to 5	208	XXXXXXXXXXXXXXXXXXXXXX
5 to 7	103	XXXXXXXXXXX
7 to 9	56	XXXXXX
9 to 11	11	X
11 to 13	8	X
13 to 15	0	
15 to 17	0	
17 to 19	0	
>19	0	

Number of Data Pairs: 1,233;
Correlation Coefficient: 0.99;
Mean Difference (ppb): 1.77;
Standard Deviation of Differences (ppb): 3.20;
Number of Absolute Differences > 20: 0;
Number of Test Days: 55.

Figure 27. Frequency distribution of differences in hourly ambient air readings between the Philips PW 9771 and the average of simultaneous readings from Bendix 8002 and Dasibi 1003-AH during Phase II Test after installation of new Rhodamine B disc. All readings corrected for zero and span drift.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN ppb:

ppb Range	Data Pairs	
<-19	0	
-19 to -17	0	
-17 to -15	0	
-15 to -13	0	
-13 to -11	0	
-11 to -9	2	X
-9 to -7	0	
-7 to -5	27	XXX
-5 to -3	37	XXXX
-3 to -1	180	XXXXXXXXXXXXXXXXXXXX
-1 to 1	238	OOOOOOOOOOOOOOOOOOOOOOOO
1 to 3	349	XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
3 to 5	203	XXXXXXXXXXXXXXXXXXXX
5 to 7	114	XXXXXXXXXXXX
7 to 9	57	XXXXXXX
9 to 11	19	XX
11 to 13	6	X
13 to 15	1	X
15 to 17	0	
17 to 19	0	
>19	0	

Number of Data Pairs: 1,233;
Correlation Coefficient: 0.99;
Mean Difference (ppb): 1.81;
Standard Deviation of Differences (ppb): 3.43;
Number of Absolute Differences > 20: 0;
Number of Test Days: 55.

Figure 28. Frequency distribution of differences in hourly ambient air readings between the Philips PW 9771 and average of simultaneous readings from Bendix 8002 and Dasibi 1003-AH during Phase II Tests after installation of new Rhodamine B disc. Philips PW 9771 readings not corrected for zero and span drift.

Manufacturer's Recommended Maintenance

Operation	Frequency
Replace Rhodamine B disc, zero filter 1, contents of conditioner and sample tubes.	Every 3 mo.
Clean the mixing section and sampler PW 9733/00.	Every 3 mo.
Maintain sample pump by replacing diaphragms and checking vacuum pressure.	Every 3 mo.
Replace ozone scrubber and dust filter 1 and 2.	Every 6 mo.
Maintain sample pump by performing 3 mo schedule and cleaning silencer.	Every 6 mo.
Maintain sample pump by performing 6 mo schedule, replacing pump crank, and checking pump motor bearings.	Every 12 mo.
Replace contents of zero filter 2.	Every 12 mo.

Malfunction

Rhodamine B discs exhausted on 11/10/77, 1/9/78, 3/6/78, 6/10/78.

A minor sample pump failure on 2/13/78 was due to a loose connection on pump bellows. Tightening the set screw corrected the problem.

General Comments

The effect of an exhausted Rhodamine B disc can be seen in the frequency distributions. Figure 25 shows a broadened distribution for an exhausted disc while Figure 27 shows a tighter one for a new disc. Each disc was exhausted in ≈2 mo--one month prior to the manufacturer's recommended time of replacement. In one case, delivery of new disc required 35 days.

The instrument required ≈2 h to stabilize in going from ambient to upper range span gas. Initial calibration pointed out minor nonlinearity in the upper range if the full stabilization period was not allowed.

DASIBI MODELS 1003-AH, 1003-PC, 1003-RS

Figure 29. Dasibi Models 1003-AH, 1003-PC, and 1003-RS (EQOA-0577-019) Ozone Analyzer. Dasibi Environmental Corp., 616 E. Colorado St, Glendale, CA 91205.

General Description

The Dasibi Model 1003-AH ozone analyzer operates on the principle of UV light absorption by ozone (see Appendix A). The instrument contains two detectors located to continuously monitor UV intensity at 254 nm from the source (control) and at the end of the 71 cm sample absorption cell (sample). During a complete measurement cycle lasting 20 to 30 seconds, zero air and sample air are alternately directed to the absorption cell. During both modes of the cycle, UV intensity reaching each detector is converted to frequency signals which are totaled by counters.

Totaling the signals effectively integrates the absorption measurement, thereby increasing sensitivity and minimizing problems due to instability in the lamp or detectors during the cycle. The counters total in the forward direction (up) during the zero mode and in the reverse direction (down) during the sample mode. When the control counter indicates that an equal amount of UV radiation entered the cell during both modes of the measurement cycle, the sample counter is stopped. The value then held by the sample counter is a measure of the ozone concentration in the sample.

The AH model is the only model tested in this report. The PC model is identical except for the internal ozone generator it contains for span checks. To facilitate automatic zero and span checks, the RS model incorporates an additional Teflon solenoid valve as well as other changes in the pneumatic system and associated controls.

The instrument's equivalent designation applies when operated in either the 0 to 0.5 ppm or 0 to 1.0 ppm range at 105 to 125 VAC and at 20 to 30 °C (68 to 86 °F).

TABLE 5. DASIBI 1003-AH LABORATORY PERFORMANCE TEST RESULTS

Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.005	0.002	0.001
Noise – 80% URL	ppm	0.005	0.002	0.001
Lower detectable limit	ppm	0.01	0.009	0.010
Interferents	ppm			
NO		±0.02	0.000	0.000
SO_2		±0.02	0.001	0.007
NO_2		±0.02	<0.001	0.000
Total		≤ 0.06	0.002[d]	0.007[d]
Zero drift – 12 hr	ppm	±0.02	0.007[d]	0.001[d]
Zero drift – 24 hr	ppm	±0.02	0.001[d]	0.002[d]
Span drift – 20% URL	%	±20.0	0.89[d]	3.05[d]
Span drift – 80% URL	%	±5.0	1.09[d]	2.20[d]
Lag time	min	20	0.6	0.2
Rise time	min	15	0.6	1.1
Fall time	min	15	0.3	0.8
Precision – 20% URL	ppm	0.010	<0.001	0.001
Precision – 80% URL	ppm	0.010	0.002	0.001

[a]From EPA equivalency regulations, 40 CFR Part 53.
[b]Average, from manufacturer's application for equivalency determination.
[c]Average, from EPA Phase I postdesignation tests, S/N 1829.
[d]Average of absolute values.

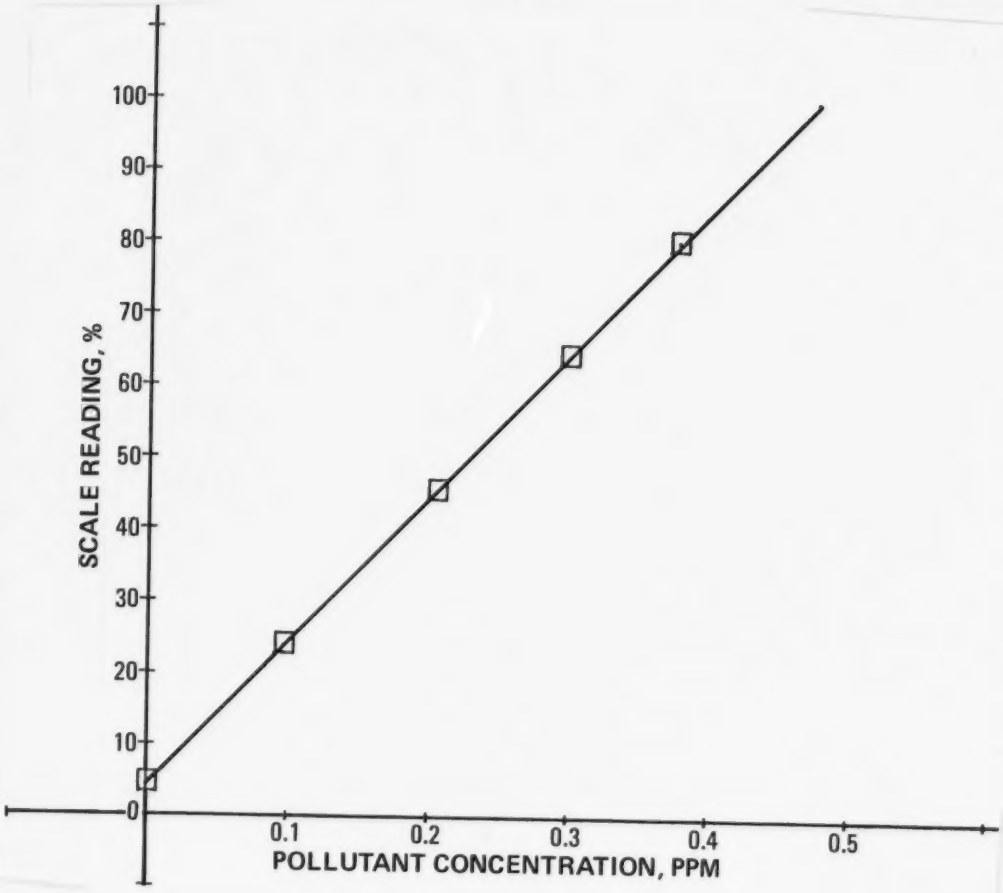
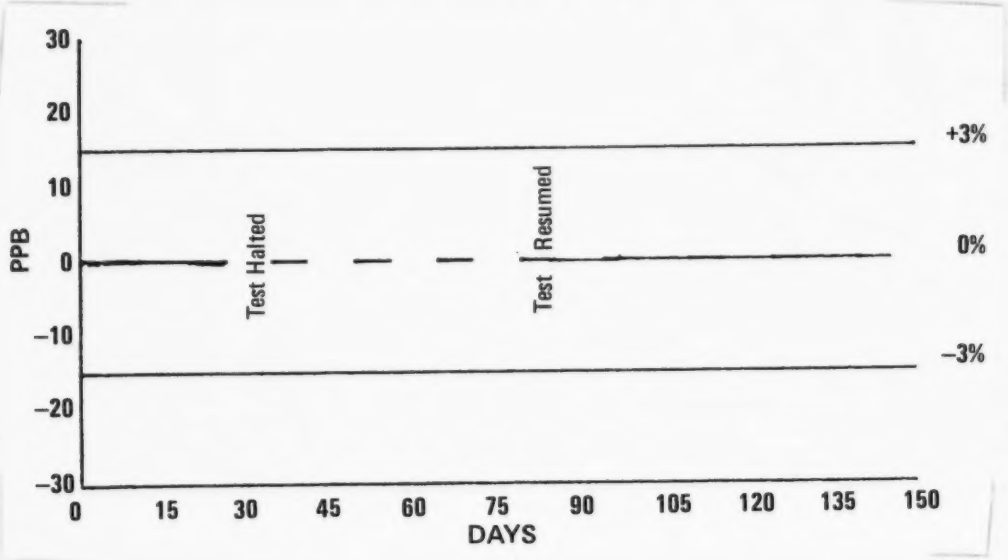


Figure 30. Typical calibration curve for Dasibi 1003-AH. Date: 9/27/78; curve drawn according to Y=MX+A where slope (M)=201.305, zero (A)=4.425; correlation coefficient (R) =1.000.

Zero Drift

Ave. Drift, ppb/day: 0.00



Span Drift

Ave. Drift, %/day: 0.03

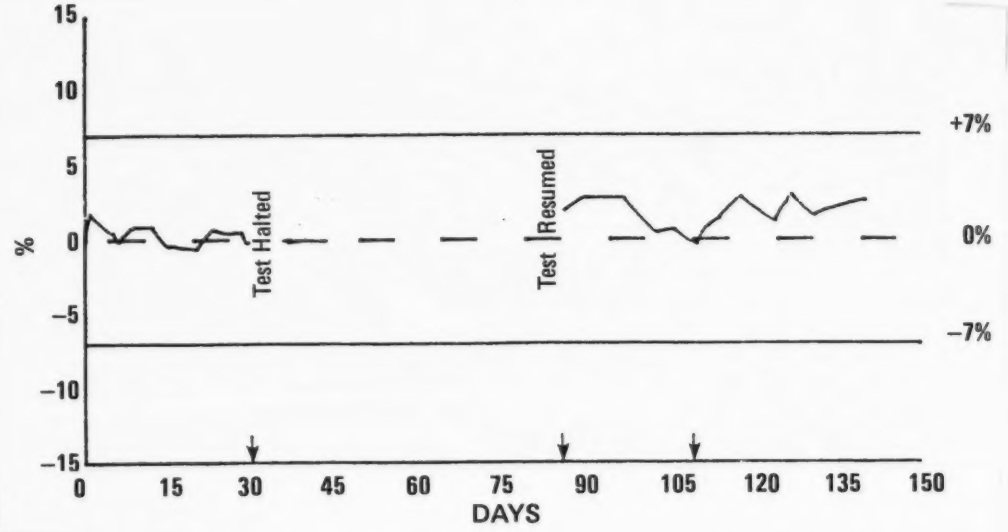


Figure 31. Zero and span drift data during Phase II Test. Nominal zero: 5.0% scale; nominal slope: 200%/ppm.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN ppb:

ppb Range	Data Pairs	
<-19	0	
-19 to-17	0	
-17 to-15	0	
-15 to-13	3	X
-13 to-11	0	
-11 to-9	2	X
-9 to-7	0	
-7 to-5	59	XXXXX
-5 to-3	175	XXXXXXXXXXXX
-3 to-1	466	XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
-1 to 1	523	OOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOO
1 to 3	488	XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
3 to 5	137	XXXXXXXXXX
5 to 7	33	XXX
7 to 9	10	X
9 to 11	2	X
11 to 13	2	X
13 to 15	0	
15 to 17	0	
17 to 19	0	
>19	0	

Number of Data Pairs: 1,900;
Correlation Coefficient: 0.99;
Mean Difference (ppb): -0.11;
Standard Deviation of Differences (ppb): 2.72;
Number of Absolute Differences > 20: 0;
Number of Test Days: 88.

Figure 32. Frequency distribution of differences in hourly ambient air readings between the Dasibi 1003-AH and average of simultaneous readings from Bendix 8002 and Philips PW 9771 during Phase II Test. All readings corrected for zero and span drift.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN ppb:

ppb Range	Data Pairs	
<-19	0	
-19 to-17	0	
-17 to-15	0	
-15 to-13	3	X
-13 to-11	0	
-11 to-9	2	X
-9 to-7	0	
-7 to-5	62	XXXXX
-5 to-3	169	XXXXXXXXXXXX
-3 to-1	475	XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
-1 to 1	513	OOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOO
1 to 3	499	XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
3 to 5	131	XXXXXXXXXX
5 to 7	33	XXX
7 to 9	10	X
9 to 11	2	X
11 to 13	1	X
13 to 15	0	
15 to 17	0	
17 to 19	0	
>19	0	

Number of Data Pairs: 1,900;
Correlation Coefficient: 0.99;
Mean Difference (ppb): -0.11;
Standard Deviation of Differences (ppb): 2.71;
Number of Absolute Differences > 20: 0;
Number of Test Days: 88.

Figure 33. Frequency distribution of differences in hourly ambient air readings between the Dasibi 1003-AH and average of simultaneous readings from Bendix 8002 and Philips PW 9771 during Phase II Test. Dasibi 1003-AH readings not corrected for zero and span drift.

Manufacturer's Recommended Maintenance

Operation	Frequency
Replace sample pump diaphragm.	Every 6 mo or when sample flow at 2 L/min cannot be maintained.
Replace solenoid valve.	Annually or as necessary.
Replace UV lamp.	Annually.
Replace cooling blower.	As necessary or in ≈3 yr.
Replace front panel display.	As necessary.
Clean optics system.	When sample and control frequency deem necessary.
Blow dirt off electronic components.	As necessary from visual inspection.
Perform leak test.	After each optics cleaning or solenoid or scrubber change.
Replace particulate filter.	When the difference between normal operation and operation bypassing the filter results in a 10% response difference.

Malfunctions

No malfunctions occurred during postdesignation testing.

General Comments

After 30 days of Phase II testing, the Philips was shut down while awaiting new Rhodamine B discs. Rather than continue the study on the remaining two analyzers in the test group, the operator halted the study until the Philips was repaired. The Dasibi, which was not powered down, was recalibrated when the study resumed.

Phase III on Dasibi 1003-AH analyzer

During March 1977 and prior to Phase I and II testing, a special purpose test was performed on four Dasibi 1003-AH analyzers. A test similar to the Subpart C consistent relationship test (defined in 40 CRF Part 53) was performed at two environmental monitoring sites located in the Mobile, AL area. At each site, two Dasibi analyzers and one reference method analyzer were installed, calibrated, and operated in accordance with the manufacturer's recommendations, Subpart C requirements, and accepted air monitoring practices. A planned deviation from the Subpart C procedure was implemented to increase the statistical acceptability of the results. The monitoring requirements were altered from a series of 1 h tests in which 14 data points were collected and compared, to a 250 to 300 h test in which all points were collected and compared. At each site, one Dasibi was operated with a Teflon sample inlet filter while the other operated without a filter to determine if there was a filter-related difference.

At the conclusion of the testing, all responses were corrected for zero and span drift before comparison. Hourly averages from each Dasibi were compared to the reference method and the differences were computed. The Subpart C maximum discrepancy specification of 0.02 ppm for an ozone concentration of 0.06 to 0.10 ppm was the specification used to judge the acceptability of the differences. Any hourly difference between the Dasibi and reference method in excess of 0.02 ppm was deemed a significant discrepancy.

Evaluation of 300 h of ambient data from site 1 resulted in no hourly average difference exceeding the 0.02 ppm specification. Evaluation of 250 h of ambient data from site 2 resulted in five hourly average differences exceeding the 0.02 ppm specification. These occurred on the Dasibi which was operated without a sample inlet filter; four of the failures occurred between 0700 and 0900 in the morning. Speculation on the failures pointed to sudden changes in ambient temperature, moisture content, and ozone concentrations that occurred in this time frame each morning. The absence of the sample inlet filter seemed to accentuate these conditions in the Dasibi and contributed to readings greater than the reference method.

Data from the Phase III test show that the four Dasibi operated for an equivalent period of 1100 h and differed from the reference method by > 0.02 ppm in only 5 h or 0.45% of the total monitoring period. The five failures were attributed to the variable water content of ambient air.

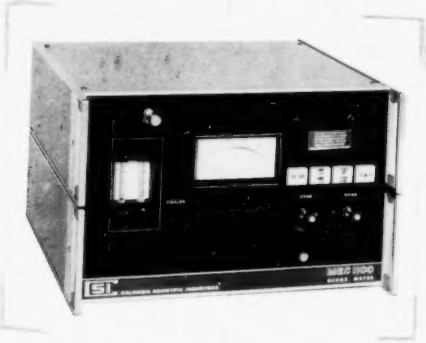


Figure 34. MEC Models 1100-1, (RFOA-1076-014), 1100-2 (RFOA-1076-015), and 1100-3 (RFOA-1076-016) Ozone Analyzer. McMillan Electronics Corp., subsidiary of Columbia Scientific Industries, 11950 Jollyville Rd, PO Box 9908, Austin, TX 78766.

General Description

The MEC series 1100 ozone analyzers operate on the ozone/ethylene chemiluminescent detection measurement principle (see Appendix A). The instruments contain a thermoelectrically cooled housing around the photomultiplier tube, which maintains temperature at 10 °C (50 °F).

The three analyzers differ in the choice of ranges available. The 1100-1 meter offers ranges from 0 to 0.5 ppm up to 0 to 10.0 ppm. The 1100-2 meter offers ranges from 0 to 0.05 ppm up to 0 to 1.0 ppm. The 1100-3 meter combines all available ranges from 0 to 0.05 up to 0 to 10.0 ppm. On all meters, two time constants are available at 1.0 or 10.0 seconds. Only the Model 1100-2 meter was tested.

The instrument's reference designation is applicable when operated on the 0 to 0.5 ppm range in ambient temperatures of 20 to 30 °C (68 to 86 °F) and a line voltage of 105 to 125 Vac. Operation is approved for both 100% ethylene and Ethychem® or equivalent ethylene/CO_2 blend (see Appendix A).

TABLE 6. MEC 1100-2 LABORATORY PERFORMANCE TEST RESULTS

Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.005	0.001	0.000
Noise – 80% URL	ppm	0.005	0.002	0.002
Lower detectable limit	ppm	0.01	0.011	0.011
Interferents	ppm			
CO_2		±0.02	0.000	0.000
H_2O		±0.02	0.002	<0.001
H_2S		±0.02	0.000	0.000
Total		≦ 0.06	0.002[d]	<0.001[d]
Zero drift – 12 hr	ppm	±0.02	<0.001[d]	0.001[d]
Zero drift – 24 hr	ppm	±0.02	0.001[d]	0.001[d]
Span drift – 20% URL	%	±20.0	1.62[d]	6.96[d]
Span drift – 80% URL	%	±5.0	1.21[d]	3.36[d,e]
Lag time	min	20	0.1	0.2
Rise time	min	15	0.2	1.1
Fall time	min	15	0.3	1.5
Precision – 20% URL	ppm	0.010	0.001	0.001
Precision – 80% URL	ppm	0.010	0.001	0.006

[a]From EPA equivalency regulations, 40 CFR Part 53.
[b]Average, from manufacturer's application for equivalency determination.
[c]Average, from EPA Phase I postdesignation tests, S/N 8184.
[d]Average of absolute values.
[e]Contains a single failure of -5.08%.

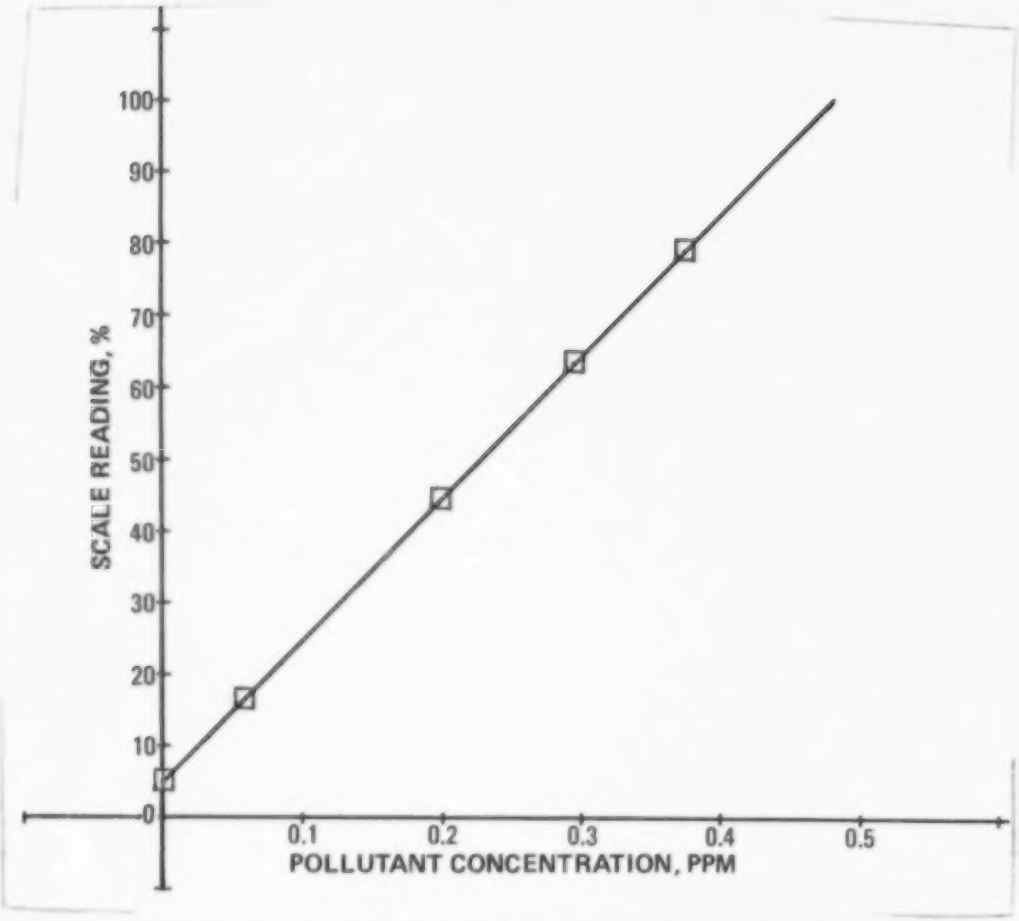


Figure 35. Typical calibration curve for MEC 1100-2. Date: 9/25/78; curve drawn according to Y=MX+A where slope (M)=197.613, zero (A)=5.063; correlation coefficient (R)=1.000.

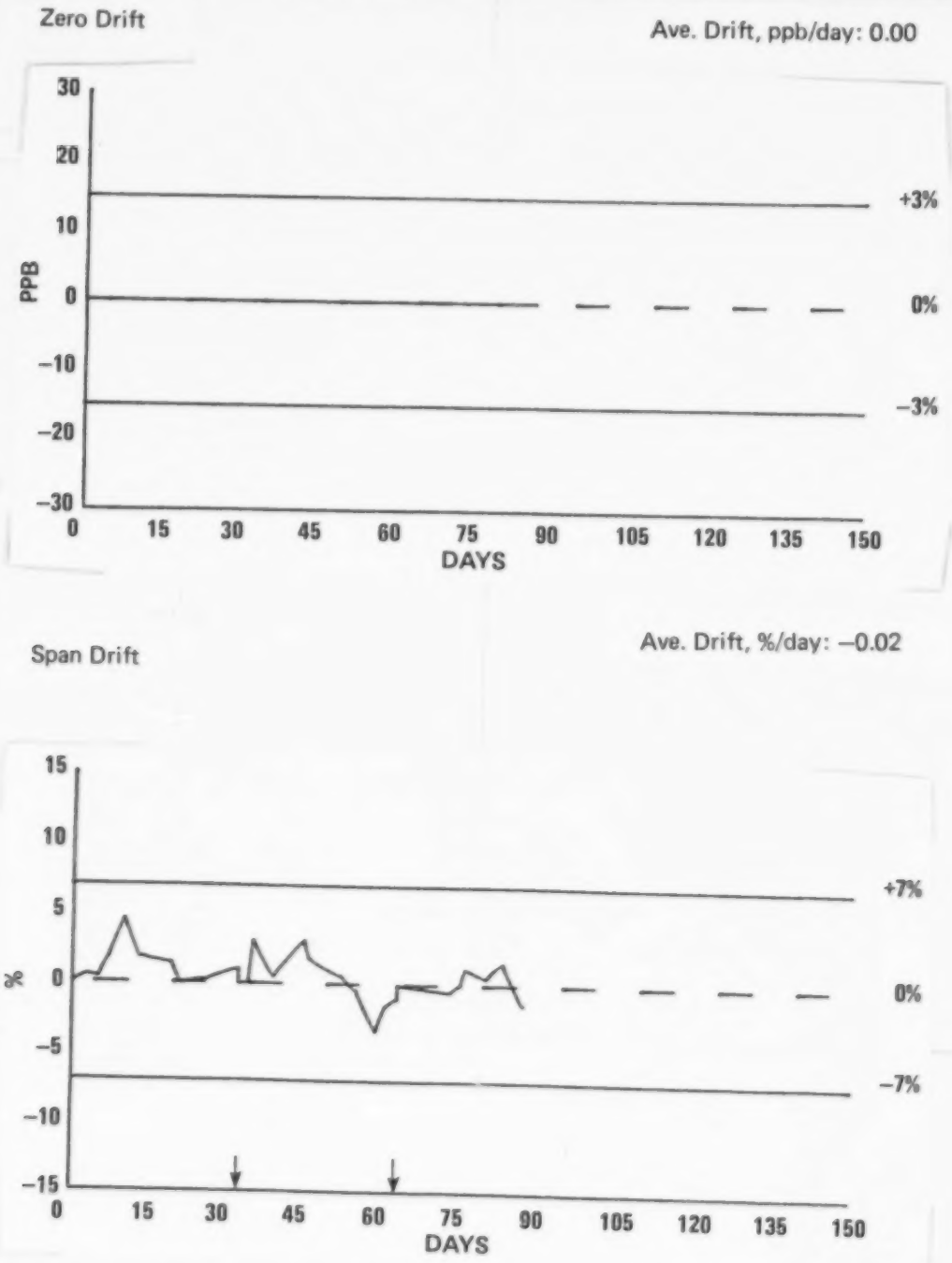


Figure 36. Zero and span drift data during Phase II Test. Nominal zero: 5.0% scale; nominal slope: 200%/ppm.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN ppb:

ppb Range	Data Pairs	
<-19	0	
-19 to -17	0	
-17 to -15	0	
-15 to -13	0	
-13 to -11	0	
-11 to -9	0	
-9 to -7	0	
-7 to -5	15	X
-5 to -3	49	XXX
-3 to -1	336	XXXXXXXXXXXXXXXXX
-1 to 1	768	OOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOO
1 to 3	548	XXXXXXXXXXXXXXXXXXXXXXXXX
3 to 5	187	XXXXXXXXXX
5 to 7	59	XXX
7 to 9	8	X
9 to 11	1	X
11 to 13	0	
13 to 15	0	
15 to 17	0	
17 to 19	0	
>19	0	

Number of Data Pairs: 1,971;
Correlation Coefficient: 0.99;
Mean Difference (ppb): 0.66;
Standard Deviation of Differences (ppb): 2.22;
Number of Absolute Differences > 20: 0;
Number of Test Days: 88.

Figure 37. Frequency distribution of differences in hourly ambient air readings between MEC 1100-2 and the average of simultaneous readings from Bendix 8002 and Beckman 950-A during Phase II Test. All readings corrected for zero and span drift.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN ppb:

ppb Range	Data Pairs	
<-19	0	
-19 to -17	0	
-17 to -15	0	
-15 to -13	0	
-13 to -11	0	
-11 to -9	0	
-9 to -7	0	
-7 to -5	12	X
-5 to -3	52	XXX
-3 to -1	308	XXXXXXXXXXXXXXXXXX
-1 to 1	701	OOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOO
1 to 3	576	XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
3 to 5	219	XXXXXXXXXXXXX
5 to 7	74	XXXX
7 to 9	27	XX
9 to 11	2	X
11 to 13	0	
13 to 15	0	
15 to 17	0	
17 to 19	0	
>19	0	

Number of Data Pairs: 1,971;
Correlation Coefficient: 0.99;
Mean Difference (ppb): 0.92;
Standard Deviation of Differences (ppb): 2.39;
Number of Absolute Differences > 20: 0;
Number of Test Days: 88.

Figure 38. Frequency distribution of differences in hourly ambient air readings between the MEC 1100-2 and the average of simultaneous readings from Bendix 8002 and Beckman 950-A during Phase II Test. MEC 1100-2 readings not corrected for zero and span drift.

Manufacturer's Recommended Maintenance

Operation	Frequency
Replace Teflon air filter.	Weekly in a high-particulate area and monthly in a low-particulate area.
Replace the sintered ethylene filter.	Every 180 days of continuous operation.
Replace the molecular sieve desiccant cartridge.	Every 2 to 3 years or when indicator turns pink.
Replace activated charcoal cartridge.	Annually if zero and span checks are performed daily.
Replace the flow regulator protective filter and blow out the critical orifice.	Annually.
Blow dust off electrical components.	Annually.

Malfunctions

The photomultiplier tube was faulty in the initial startup on 9/29/77. See General Comments. The Ethychem® regulator was defective on 11/21/77 and was replaced. See General Comments.

General Comments

All Phase I and Phase II tests were conducted with the analyzer operating on Ethychem®. During initial startup on 9/29/77, the PM tube failed. The instrument was shipped back to the manufacturer for replacement and was returned on 11/10/77.

During Phase I testing, a high noise level was attributed to a defective Ethychem® regulator. Replacing the regulator reduced the noise.

An "Overshoot" problem (see Phase I test comments) developed during Phase I testing in which the analyzer's initial response to an upper range span gas was substantially higher than its final response level. After several hours, the response stabilized at the span gas concentration. The manufacturer stated that the overshoot problem was "typical" for this analyzer when operated on Ethychem®. A marginal failure on the 80% span drift test was attributed to the overshoot problem, which impeded the reading of "stable responses". No overshoot difficulties were encountered during Phase II testing.

BECKMAN MODEL 950-A

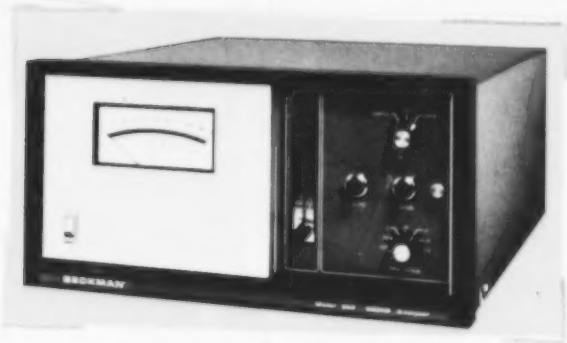


Figure 39. Beckman Model 950-A (RFOA-0577-020) Ozone Analyzer. Beckman Industries, Inc., Process Instruments Div., 2500 Harbor Blvd., Fullerton, CA 92634.

General Description

The Beckman Model 950-A ozone analyzer operates on the ozone/ethylene chemiluminescent detection measurement principle using Ethychem® or equivalent ethylene/CO_2 blend (see Appendix A). The instrument contains a scrubber to generate zero air and may be equipped with an ozone generator to generate span gas. The instrument contains a thermoelectrically cooled housing around the photomultiplier tube that maintains temperature at 6 °C (42.8 °F). Seven concentration ranges are available from 0 to 0.025 ppm up to 0 to 2.5 ppm. Two time constants are available at SLOW (≈60 sec for all ranges) and FAST (≈3 sec on concentration ranges of 0.5 ppm through 0.25 ppm and ≈30 sec for ranges 0.025 ppm through 0.25 ppm).

The instrument's reference designation is valid when operated on the 0 to 0.5 ppm range at SLOW response time with ambient temperature at 20 to 30 °C (68 to 86 °F) and line voltage between 105 and 125 Vac. Operation of the 950-A on 100% ethylene has not been certified.

TABLE 7. BECKMAN 950-A LABORATORY PERFORMANCE TEST RESULTS

Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c] Initial	Retest[g]
Noise – 0% URL	ppm	0.005	0.000	0.000	
Noise – 80% URL	ppm	0.005	0.001	0.001	
Lower detectable limit	ppm	0.01	0.009	0.011	
Interferents	ppm				
CO_2		±0.02	0.001	0.000	
H_2O		±0.02	0.001	0.001	
H_2S		±0.02	0.000	-0.001	
Total		≤ 0.06	0.002[d]	0.002[d]	
Zero drift – 12 hr	ppm	±0.02	0.003[d]	<0.001[d]	0.001[d]
Zero drift – 24 hr	ppm	±0.02	<0.001[d]	0.006[d,e]	0.001[d]
Span drift – 20% URL	%	±20.0	3.41[d]	8.23[d,f]	2.40[d]
Span drift – 80% URL	%	±5.0	1.29[d]	2.32[d]	1.88[d]
Lag time	min	20	0.3	0.2	
Rise time	min	15	1.2	1.2	
Fall time	min	15	1.2	1.3	
Precision – 20% URL	ppm	0.010	0.002	0.001	
Precision – 80% URL	ppm	0.010	0.002	0.003	

[a] From EPA equivalency regulations, 40 CFR Part 53.
[b] Average, from manufacturer's application for equivalency determination.
[c] Average, from EPA Phase I postdesignation tests, S/N 1000142.
[d] Average of absolute values.
[e] This average includes a failure of 0.021.
[f] This average includes a failure of 23.23.
[g] Retest results after replacement of the thermoelectric cooler, PM tube assembly, teflon sample line, and Ethychem® filter.

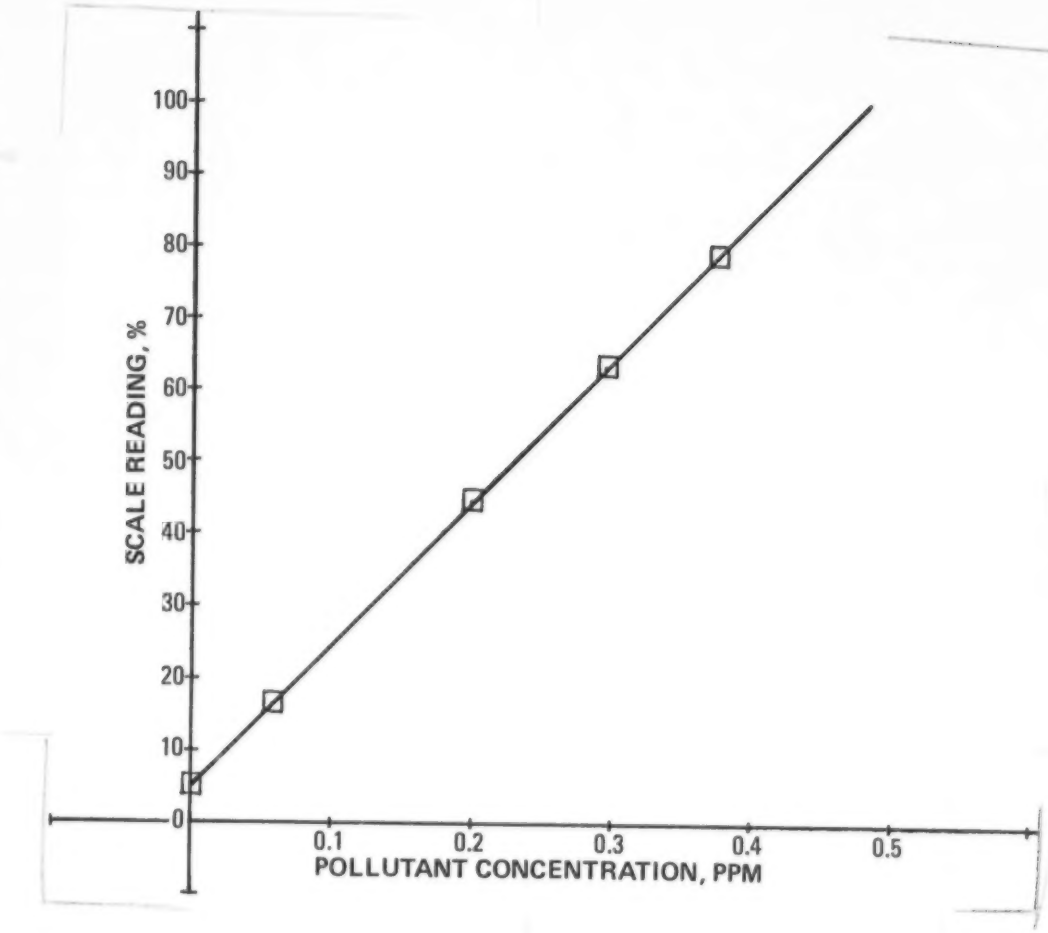
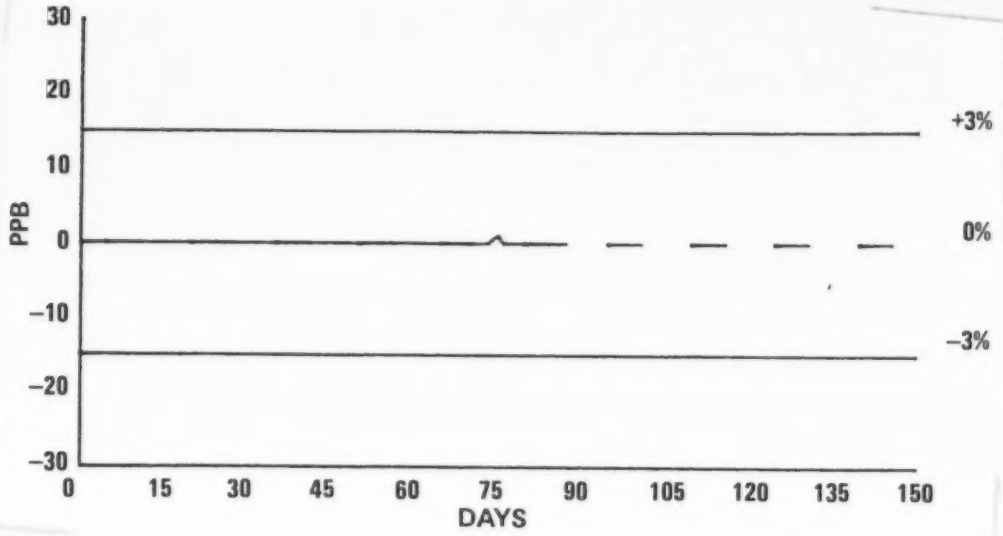


Figure 40. Typical calibration curve for Beckman 950-A. Date: 9/25/78; curve drawn according to Y=MX+A where slope (M)=197.613, zero (A)=5.063; correlation coefficient (R)=1.000.

Zero Drift

Ave. Drift, ppb/day: 0.00



Span Drift

Ave. Drift, %/day: −0.21

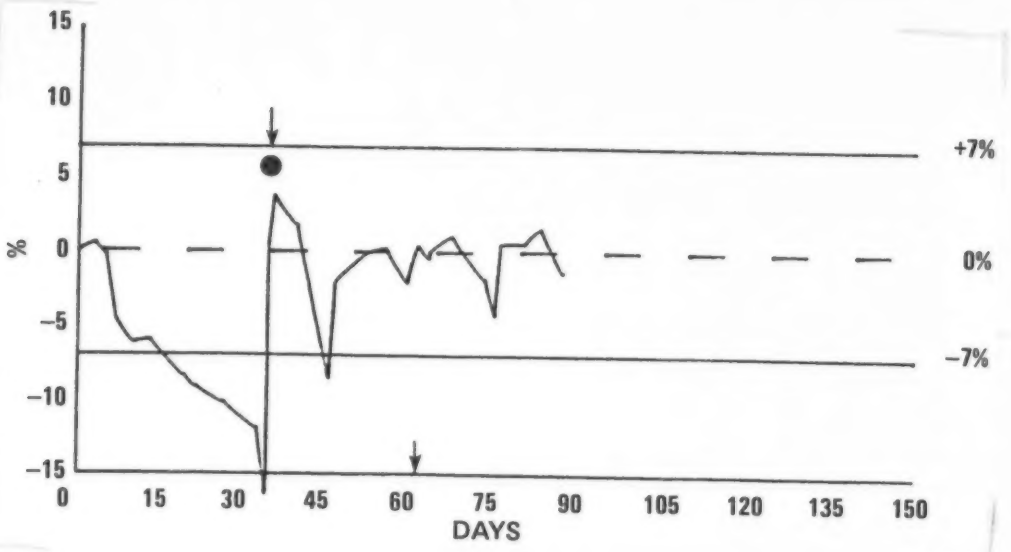


Figure 41. Zero and span drift data during Phase II test. Nominal zero: 5.0% scale; nominal slope: 200%/ppm.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN ppb:

ppb Range	Data Pairs	
<-19	0	
-19 to -17	0	
-17 to -15	0	
-15 to -13	0	
-13 to -11	0	
-11 to -9	1	X
-9 to -7	0	
-7 to -5	40	XX
-5 to -3	105	XXXXXX
-3 to -1	296	XXXXXXXXXXXXXXXX
-1 to 1	722	OOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOO
1 to 3	544	XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
3 to 5	183	XXXXXXXXXX
5 to 7	60	XXX
7 to 9	16	X
9 to 11	2	X
11 to 13	0	
13 to 15	1	X
15 to 17	0	
17 to 19	0	
>19	0	

Number of Data Pairs: 1,970;
Correlation Coefficient: 0.99;
Mean Difference (ppb): 0.54;
Standard Deviation of Differences (ppb): 2.52;
Number of Absolute Differences > 20: 0;
Number of Test Days: 88.

Figure 42. Frequency distribution differences in hourly ambient air readings between the Beckman 950-A and the average of simultaneous readings from Bendix 8002 and MEC 1100-2 during Phase II Test. All readings corrected for zero and span drift.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN ppb:

ppb Range	Data Pairs	
<-19	0	
-19 to -17	0	
-17 to -15	0	
-15 to -13	1	X
-13 to -11	1	X
-11 to -9	8	X
-9 to -7	0	
-7 to -5	59	XXXX
-5 to -3	143	XXXXXXXXX
-3 to -1	303	XXXXXXXXXXXXXXXXX
-1 to 1	665	OOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOOO
1 to 3	501	XXXXXXXXXXXXXXXXXXXXXXXXXXXXX
3 to 5	213	XXXXXXXXXXXXX
5 to 7	56	XXX
7 to 9	15	X
9 to 11	4	X
11 to 13	1	X
13 to 15	0	
15 to 17	0	
17 to 19	0	
>19	0	

Number of Data Pairs: 1,970;
Correlation Coefficient: 0.99;
Mean Difference (ppb): 0.37;
Standard Deviation of Differences (ppb): 2.80;
Number of Absolute Differences > 20: 0;
Number of Test Days: 88.

Figure 43. Frequency distributions of differences in hourly ambient air readings between the Beckman 950-A and the average of simultaneous readings from Bendix 8002 and MEC 1100-2 during Phase II test. Beckman 950-A readings not corrected for zero and span drift.

Manufacturer's Recommended Maintenance

Operation	Frequency
Replace sample inlet Teflon filter.	Monthly.
Replace ethylene capillary.	When it becomes clogged.
Clean ethylene flowmeter.	When it begins sticking.
Clean reaction chamber.	Whenever contaminated.
Replace activated carbon zero air scrubber.	Annually if analyzer zero is checked daily.
Replace sample pump components.	When unable to obtain a stable 500 cm^3/min flow rate.

Malfunctions

The photomultiplier tube (PMT) was replaced on 1/5/78 See General Comments. The thermoelectric cooler/PMT assembly was replaced on 4/19/78. See General Comments.

General Comments

All tests were conducted using Ethychem® (the analyzer is not designed to use 100% ethylene). During Phase I testing, an "overshoot" problem (see the Phase I test comments) developed in which the analyzer's initial response to an upper range span gas was substantially higher than its final response. After several hours, the response would slowly decrease and ultimately stabilize at the span gas concentration. The manufacturer's representative replaced the PMT, which lessened the severity of the problem but did not completely correct it. In addition, test failures occurred on the 24 h zero span drift and 20% URL (MSD) test. The failures were primarily linked to a malfunction in the thermoelectric cooler/PMT assembly. After replacement of the assembly, no further failures occurred.

No overshoot difficulties were encountered during Phase II testing.

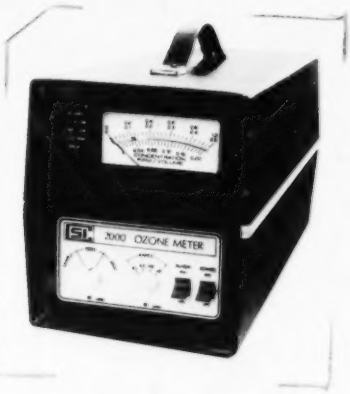


Figure 44. CSI Model 2000 (RFOA-0279-036) Ozone Meter. Columbia Scientific Industries, 11950 Jollyville Rd, PO Box 9908, Austin, TX 78766.

General Description

The CSI Model 2000 ozone meter operates on the ozone/ethylene chemiluminescent detection measurement principle (Appendix A). The instrument contains a thermoelectrically cooled housing around the photomultiplier tube that maintains temperature at 25 °C (77 °F).

A predominant feature of this meter is its portability. A self-contained cylinder that can be refilled with ethylene and a rechargeable battery pack are standard equipment. The manufacturer states that 4000-5500 kPa (600 to 800 psig) ethylene is generally sufficient for a 9 h day of operation. The battery life between chargings varies from 4 to 9 h depending on temperature and initial battery charge.

Four concentration ranges are available from 0 to 0.1 ppm up to 0 to 1.0 ppm. No selectable time constants are available. The reference designation is applicable when the instrument is operated with the inlet air sample filter (P/N M951-8027) installed, the range selected is 0 to 0.5 ppm full scale, ambient temperature is 20 to 30 °C (68 to 86 °F), and line voltage is 105 to 125 Vac. At this time, no postdesignation testing has been performed.

TABLE 8. CSI MODEL 2000 LABORATORY PERFORMANCE TEST RESULTS

Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.005	0.000	
Noise – 80% URL	ppm	0.005	0.002	
Lower detectable limit	ppm	0.01	0.010	
Interferents	ppm			
CO_2		±0.02	<-0.001	TESTING
H_2O		±0.02	0.001	NOT YET
H_2S		±0.02	0.000	PERFORMED
Total		$\leq$ 0.06	0.002[d]	
Zero drift – 12 hr	ppm	±0.02	0.004[d]	
Zero drift – 24 hr	ppm	±0.02	0.003[d]	
Span drift – 20% URL	%	±20.0	2.71[d]	
Span drift – 80% URL	%	±5.0	1.37[d]	
Lag time	min	20	< 0.1	
Rise time	min	15	< 0.5	
Fall time	min	15	< 0.5	
Precision – 20% URL	ppm	0.010	0.001	
Precision – 80% URL	ppm	0.010	0.001	

[a]From EPA equivalency regulations, 40 CFR Part 53.
[b]Average, from manufacturer's application for equivalency determination.
[c]Average, from EPA Phase I postdesignation tests.
[d]Average of absolute values.

THERMO ELECTRON MODEL 49

Figure 45. Thermo Electron Model 49 (EQOA-0880-047) Ozone Analyzer. Thermo Electron Corporation, 108 South Street, Hopkinton, MA 01748.

General Description

The Thermo Electron Model 49 UV Photometric Ambient Ozone analyzer operates on the principle of UV light absorption by ozone (see Appendix A). The instrument uses a dual cell arrangement with two UV sources and two UV detectors. The UV sources are low pressure mercury vapor lamps which have 95% of their light output at the 254 nm line and no output at the ozone-forming 185 nm line. Solar blind vacuum photodiodes (i.e., sensitive to UV light but not visible light) which have virtually no sensitivity above 300 nm are used as detectors, assuring that more than 99.5% of the detected signal is due to the 254 nm line.

During the first half of the measurement cycle, zero air is directed to cell A for a zero reading (I_o) and sample air is directed to cell B for the sample reading (I). These readings are stored. For the last half cycle, zero air goes to cell B and sample air to cell A. The complete cycle is 20 seconds long, and during both modes the UV intensity reaching each detector is converted to frequency signals which are totaled by counters. Totaling the signals effectively integrates the absorption measurement, thereby increasing sensitivity and minimizing problems due to instability in the lamp or detectors during the cycle.

After each half cycle the microcomputer in the Model 49 uses the stored I and I_o readings to calculate the ozone concentration, making automatic corrections for changes in temperature and pressure. These ozone concentrations are displayed digitally on the front panel and in analog form at the recorder output. The dual cell, flow switching arrangement provides increased sensitivity and better rejection of interferences and errors due to lamp fluctuation or drift.

The instrument's equivalent method designation applies when operated in either the 0 to 0.5 ppm or 0 to 1.0 ppm range at 105 to 125 Vac and at 20 to 30 °C (68 to 86 °F).

TABLE 9. THERMO ELECTRON MODEL 49 LABORATORY PERFORMANCE TEST RESULTS

Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise -0% URL	ppm	0.005	<0.001	
Noise - 80% URL	ppm	0.005	0.001	
Lower detectable limit	ppm	0.01	0.096	
Interference	ppm			
SO_2		±0.02	0.002	TESTING
H_2O		±0.02	0.002	NOT YET
m-xylene		±0.02	0.001	PERFORMED
Total		≤0.06	0.007[d]	
Zero drift - 12 hr	ppm	±0.02	0.002[d]	
Zero drift - 24 hr	ppm	±0.02	<0.001[d]	
Span drift - 20% URL	%	±20.0	3.93[d]	
Span drift - 80% URL	%	±5.0	0.87[d]	
Lag time	min	20.0	0.2	
Rise time	min	15.0	0.3	
Fall time	min	15.0	0.4	
Precision - 20% URL	ppm	0.010	0.001	
Precision -80% URL	ppm	0.010	0.002	

[a]From EPA equivalency regulations, 40 CFR Part 53.
[b]Average, from manufacturer's application for equivalency determination.
[c]Average, from EPA Phase I postdesignation tests.
[d]Average of absolute values.

APPENDIX A

MEASUREMENT PRINCIPLES FOR OZONE ANALYZERS

EPA designated ozone analyzers operate according to one of the following measurement principles:

1. Ozone/Ethylene Chemiluminescent Detection (Reference Methods)

2. Ozone/Rhodamine B Chemiluminescent Detection (Equivalent Methods)

3. Ultraviolet Light Absorption by Ozone (Equivalent Methods)

Brief descriptions of these measurement principles are presented in this section to compare the similarities and differences among the analyzers.

OZONE/ETHYLENE CHEMILUMINESCENT DETECTION

This measurement principle is based on the photometric detection of the chemiluminescence (light produced by a chemical reaction) resulting from the flameless gas phase reaction of ethylene (C_2H_4) with ozone (O_3). The sample gas containing ozone is mixed with excess ethylene (bottle gas supplied to the instrument) to generate excited formaldehyde (HCHO*) molecules. The excited formaldehyde molecules decay immediately to the ground energy state, releasing energy in the form of light in the 300 to 600 nm region, with maximum intensity at 430 nm. The light energy is measured by a photomultiplier tube (PMT), which produces an output current proportional to the light intensity. The current, converted to voltage and conditioned as necessary by the electronic circuits, becomes the analyzer's output signal.

The determination of ozone concentration is based on the relationship in which the light intensity, released during the decay of the formaldehyde species, is directly proportional to the ozone concentration of the sample gas. The reactions are as follows:

$$2O_3 + 2C_2H_4 \rightarrow 2C_2H_4 \cdot O_3 \rightarrow 4HCHO^* + O_2$$
$$HCHO^* \rightarrow HCHO + h\nu$$

There are no ambient species that act as interferents to the reaction. Temperature, however, can affect the noise level of the PMT, and thus the temperature of the PMT and adjacent electronics is usually controlled. Manufacturers disagree on the temperatures at which the PMT assembly should be maintained, the range being 5 to 25 °C (41 to 77 °F), depending on the manufacturer.

Some analyzers use the process of "chopping" the light energy that the PMT receives. The light is modulated by the use of a fan-like blade chopper rotating at a constant speed to alternately block and pass the light to the PMT. The claimed advantage of chopper-stabilized electronics is the reduction of zero drift due to changes in the photomultiplier dark current without the need for highly stable PMT temperature control.

Due to the flammability of ethylene, some manufacturers suggest the use of an ethylene-carbon dioxide blend such as Ethychem® (Linde) instead of 100% ethylene when the monitoring device is to be used in a public facility. This blend is a liquified, nonflammable mixture of approximately 9% ethylene and 91% CO_2. The chemiluminescent reaction is the same; however, gas consumption is considerably higher to account for the reduced ethylene concentration. The proportions of ethylene and CO_2 supplied by the blend change somewhat as the mixture is consumed from the cylinder. This changes the sensitivity of the analyzer. Consequently, the analyzer should be recalibrated more frequently. The concentrations of ethylene supplied by the blend is also changed by the temperature of the cylinder, which must therefore be maintained reasonably constant during use.

OZONE/RHODAMINE B CHEMILUMINESCENT DETECTION

The need for ethylene can be circumvented althogether by using a disc containing an organic dye, Rhodamine B, and gallic acid to react with ozone. In this chemiluminescent reaction, ozone laden sample air passes over the disc and reacts to form oxygen and a derivative of gallic acid. The gallic acid derivative, in turn, reacts with the Rhodamine B to produce excited Rhodamine B. Reduction of the excited Rhodamine B to the ground energy level results in the emission of light energy in the range of 550 to 650 nm with the maximum at 580 nm. The light is sensed by the PMT, which produces a current and output similar to that described for the ozone/ethylene process.

The Rhodamine B disc has a characteristic hysteresis which requires compensation during analyzer operation. In essence, this effect produces a variable signal to the detector depending upon the previous history of the disc. If the disc has been exposed to low ozone concentrations (e.g., 0.01 ppm), the initial response to a higher concentration such as 0.400 ppm ozone will be < 0.400 ppm. After a period of exposure to this higher concentration, the response will become stabilized. Similarly, if conditioned at 0.400 ppm, the initial response to 0.01 ppm ozone will be > 0.01 ppm. After conditioning at this lower concentration, the response will again become stabilized.

The hysteresis can be compensated for by a cyclic operating mode which includes zero and span checks during each measurement cycle. The analyzer sequentially determines background, sample, and span concentrations. In the background phase, sample air is directed through an ozone scrubber prior to injection into the ozone detector. This phase is ≈40 sec long and results in a background signal, which is stored. The sampling phase occurs next by diverting sample flow around the ozone scrubber and directly into the ozone detector. This phase is ≈20 sec and results in the sample signal, which is also stored.

The span phase completes the cycle by diverting sample flow through a conditioner, zero filter, and an ozone source before reaching the ozone detector. This last phase is ≈20 sec and results in a stored span signal. At the conclusion of the three phases of the cycle, the three electronic signals are used to calculate the correct ozone concentration of the sample. This continual referencing to establish the background and span gas response effectively compensates for the hysteresis effect.

ULTRAVIOLET LIGHT ABSORPTION BY OZONE

This principle is based on the absorption of ultraviolet (UV) light by the ozone molecule and the subsequent measurement of the reduction of UV intensity by photometry. The degree to which UV radiation is reduced depends on the pathlength of the UV sample cell, the ozone concentration introduced into the sample cell, and the wavelength of the UV light. The degree of light attenuation is expressed by the Beer-Lambert law shown below.

$$I = I_o \exp(-\alpha \ell C)$$

where

I_o = the light intensity at zero ozone concentration,
I = the light intensity after attenuation by ozone,
C = the ozone concentration,
ℓ = the pathlength, and
α = the specific ozone absorption coefficient.

The sample is introduced into an absorption cell in the path of light from a stable UV source. The UV source is a low pressure cold cathode mercury vapor lamp fitted with a Vycor sheath to filter out radiation with a wavelength < 254 nm. A solar blind photodetector, located at the opposite end of the sample cell, measures the reduction in UV intensity (at wavelengths < 300 nm) due to the presence of ozone in the sample cell. To compensate for possible irregularities in output, another photodetector may be used to monitor the UV source intensity.

Operation of the analyzer is cyclic. The sample air is first directed through an ozone filter (manganese dioxide) to remove ozone. The resulting zero air enters the absorption (sample) cell to establish a zero reference light intensity (I_o). The monitor then automatically directs the sample air to bypass the filter and enter the sample cell directly for measurement of the attenuated light intensity (I). The difference is related to the ozone concentration according to the Beer-Lambert Law. Ozone in the sample stream can be measured continually by alternately measuring the light level at the sample detector with ozone removed and then with ozone present.

Although it is possible to calculate the theoretical ozone concentration from the Beer-Lambert expression, the resulting measurement is inherently accurate only when the instrument meets the requirements of a calibration photometer (described in Appendix D of 40 CFR Part 50). However, like any type of ozone analyzer used for routine ambient monitoring, a UV analyzer must be calibrated against a suitable O_3 standard.

Interferent tests are specified for NO, NO_2, and SO_2. Additional potential interferences to the photometric detection of ozone are heavy hydrocarbons, mercury vapor, and water.